Development of Synthetic Soils for Sorption
Mass Transfer Model Validation

THESIS

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AFIT/GEE/ENV/96D-02

DEPARTMENT OF THE AIR FORCE
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Captain Thomas P. de Venoge

Presented to the Faculty of the Graduate School of Engineering

of the Air Force Institute of Technology

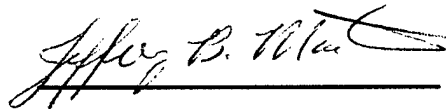In Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Engineering and Environmental Management

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Air Education and Training Command

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Thomas P. de Venoge

Captain, United States Air Force

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ABSTRACT

Existing sorption mass transfer models often fail to accurately describe sorption of organic contaminants at the grain scale because of an inability to adequately define the diffusion domain. Improving this capability may lead to better exposure and risk estimates for groundwater pollutants and improved clean-up operations. A proposed model by Heyse (1994) developed for this purpose required testing to determine model validity. The testing method selected involved using a synthetic soil of known geometries such that the distribution of sorption sites is known. After preliminary experiments confirming suitability of the synthetic soil chosen (paraffin), a protocol was developed describing methods to ensure consistent chemical and physical properties of the soil. Batch sorption experiments with the synthetic media were performed and produced sorption rate data to be used in comparison against predicted rates by the model. Fitted distributions of sorption sites predicted by the model from sorption rate data was compared to the real distribution obtained by controlling sorbent geometries in the batch experiments. Comparison allowed determination of model performance in fitting the known distributions.

Three questions described the focus of this study:

1.) What protocols are necessary to ensure consistent chemical and physical properties of a synthetic media for sorption studies?

2.) Can the proposed model predict the known shape parameters describing the real frequency distribution of sorption sites by using the rate data obtained from sorption studies?

3.) Can the model be validated?

Model performance was very encouraging for simulations involving simultaneous fitting of two shape parameters. These simulations resulted in sorption site distributions very similar to the known distributions. This model is an improvement over other diffusion models where geometries are assumed to be spherical. Prediction of real soil sorption site distributions may be possible.

I. INTRODUCTION

Overview of Research Interest

Groundwater contamination on Air Force installations is often the result of hydrophobic organic compounds (HOCs) such as aircraft fuels, solvents, and transformer oils. Once in the subsurface, organic components of these mixtures partition between the aqueous (dissolved) and nonaqueous phase and diffuse into soil organic matter (SOM), pore spaces, or adsorb to mineral surfaces in aquifer materials. These partitioning and adsorption processes are collectively referred to as sorption. Subsurface contaminant fate and transport mechanisms must be understood to determine ultimate groundwater concentrations of these chemicals and locations of contaminant plumes. For SOM, partitioning infers that a chemical species dissolves into the organic matter and is of interest because the rates at which HOCs partition may determine transport times and eventual impact at would-be receptor wells. This affects estimates for exposure times and results of risk analyses. Rates of sorption and desorption are significant factors in determining availability of contaminants for microbial degradation and the success of remedial action alternatives that employ a bioremediation strategy (Skow and Hutson, 1992; Skow and Alexander,1992; Schwarzenbach et al., 1993; Pignatello and Xing, 1996).

Modeling of contaminant transport at hazardous waste sites can involve the use of simplifying assumptions, such as the local equilibrium assumption (LEA). The LEA states that the solute is at equilibrium between all phases at any point in space and is used to simplify the transport equations (Valocchi, 1986; Goltz and Oxley, 1991).

Contaminants partition between the dissolved and solid phases at a certain ratio depending on the characteristics of the contaminant and the aquifer material. These characteristics include the activity coefficients of the sorbate in water and in the sorbed phase, or the dissolved and organic phase fugacities of the sorbate. Because water is a polar molecule and HOCs are nonpolar, molecular forces drive HOCs to assimilate with a similar substance such as SOM. Although not completely nonpolar, SOM have significant nonpolar moieties. At equilibrium, the aqueous and sorbed phase fugacity or chemical potential of a contaminant are equal (Brusseau and Rao, 1989a; Rao et al., 1985). LEA states that the process of a contaminant partitioning between sorbed and dissolved phase is instantaneous. This approach has resulted in overestimates of arrival times of contaminant plumes and underestimates of expected groundwater cleanup times resulting from long term tailing of contaminants as HOCs slowly desorb from the aquifer solids (Goltz and Oxley, 1991). Slow, long-term desorption is not described by LEA.

Remedial action alternatives based on extraction of contaminated water (pump and treat) often do not succeed and are over budget because of sorption nonequilibrium that results in long-term tailing. Tailing prolongs remedial action cleanup times and increases costs because increased volumes of water must be pumped and subsequently treated.

The limited applicability of the LEA is evident in findings of researchers studying sorption nonequilibrium (Valocchi, 1986; Brusseau et al., 1989). Several models describing grain-scale, rate limited sorption of organic chemicals are recognized as better representations of reality than the LEA affords. Because diffusion is probably the governing mass transfer process for HOCs at the grain scale, these models are

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either diffusion models or models approximating diffusion as a first-order process (Parker and Valocchi, 1986; Wu and Gschwend, 1986; Brusseau and Rao, 1989a; Ball and Roberts, 1991a). First order, one or two site models do a poor job in successfully describing the long term tailing of contaminants while diffusion models and multisite first order models perform better. This frequent failure may be the result of the inability of the models to describe sorption sites at long path lengths (Heyse, 1994). Research on improving the models describes the sorption sites as a frequency distribution along a path length. Similarly, a frequency distribution of first-order rate constants may be used. Both approaches aim to improve the description of sorption sites while not requiring any more fitting parameters. This approach may do a better job of modeling the long term tailing resulting from slow desorption of contaminants from aquifer materials (Heyse,1994) by describing sorption sites at long path lengths or accounting for very slow first order rate constants. Heyse's (1994) research with multisite models using natural soils confirms model ability to reproduce breakthrough curves from sorption experiments. However, this alone does not confirm model validity.

One approach to show model validity is to determine if the model assumptions are valid. Similarly, the ability to predict model parameters from rate data is a strong indicator of model performance. This approach may involve use of a soil of known physical and chemical characteristics. Prior knowledge of the physical structure and geometry of the sorbent material is used to assess the model's ability to predict a physical reality versus a convenient set of numbers. Knowing the distribution of SOM at the grain scale is virtually impossible (Rebhun, 1991; Young and Ball, 1995) so researchers use synthetic media and control the geometries of the individual particles (Rao et al, 1980a; Skow and Alexander, 1992; Heyse 1994). Methods and protocols

for obtaining consistent chemical properties and geometries of synthetic soil particles must be developed. Heyse's (1994) research using paraffin as a synthetic soil indicated a need for such a protocol to obtain consistent and reproducible results (Heyse, 1994).

This research effort will generate the data needed and take the steps to test the hypothesis that a multisite mass transfer model is a possible candidates for improved modeling of sorption nonequilibrium. Batch sorption experiments with synthetic media and an organic solute are used to generate sorption rate data. A multisite model is fit to the data to determine ability to predict known sorbent geometries, leading to model validation and applicability to natural soils.

Research Objectives

Develop Synthetic Soil with Consistent Sorption Properties

The goal of this part of the research effort involved identification of a synthetic soil (sorbent) for use in sorption mass transfer studies of HOCs. The synthetic soil must exhibit consistent sorption properties such that results from replicate batch experiments are consistent and results reproducible. The size and shape of the individual soil particles must be consistent so that the diffusion domain can be accurately described. This information is necessary for the model validation part of the research and will describe model fitting parameters. The synthetic media must not interfere with analytical procedures, must provide for a linear isotherm, and experience no substantial decay or reactivity with the solute. Lastly, the synthetic material must be

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tested and shown to exhibit consistent sorption behavior before sorption mass transfer studies for model validation can begin.

Validation of Multisite Mass Transfer Model

The goal for this part of the research was to determine whether the model could predict the distribution of sorption sites for the synthetic soil using rate data from batch experiments. Because the synthetic soil geometry is known, the maximum diffusion path length, δ_{max}, and the shape factor, λ, are known. The objectives are to determine the following:

1.) Whether rate data can be used to accurately predict up to two fitting parameters, and

2.) If one average shape can be used to accurately describe a mixture of sizes of the same sorbent.

If the model can predict the known fitting parameters that describe the frequency distribution of sorption sites, and match the rate data for batch experiments, this is a strong indicator that the model is capable of describing more complex soil systems such as found in natural soils.

Organization of Thesis

Chapter II contains a review of literature on current knowledge of sorption mechanisms, kinetics, and models. Materials, methods and equipment used are discussed in Chapter III. This includes protocols used in developing and testing synthetic soils, performing batch experiments, and computer simulations using batch results for testing the proposed model. Results from these experiments are also discussed in Chapter III. Chapter IV contains a summary and conclusions.

II. REVIEW OF THE LITERATURE

Overview

This chapter reviews prevalent theories for explaining sorption nonequilibrium. Deficiencies in existing sorption models are discussed and proposed improvements are presented. Use of synthetic soils is reviewed and how these soils may provide a method of validating models.

Soil Sorption Kinetics

Sorption is a generic term used to describe a process whereby chemicals partition from a dissolved aqueous phase into sorbent material or adsorb to mineral surfaces in aquifer materials. Causes and mechanisms of sorption are often unclear but may include chemical kinetics such as chemisorption, partitioning into soil pores and SOM, or surface adsorption due to charged surfaces such as with clay particles. Because HOCs are nonpolar, adsorption reactions due to charged species can be ignored. Partitioning into soil particle pores and SOM are considered to be the dominant cause of sorption of HOCs. HOC molecules bind to sorption sites in SOM by van der Waals forces while SOM binds to soil particle mineral surfaces through hydrogen bonding (Szecsody, 1988).

The ratio of the sorbed phase concentration, S, to the dissolved or solution phase concentration, C_L, is defined as the distribution coefficient, K_d. Because the sorption of HOCs into SOM is considered a partitioning process, K_d is written as the equilibrium partition coefficient, K_p, which is expressed mathematically for HOCs at equilibrium as equation (1):

$$K_p = \frac{S}{C_L} \qquad (1)$$

This value is usually obtained through laboratory batch methods but can also be estimated for HOCs by means of a regression equation, assuming there is a significant fraction of organic carbon ($\geq 0.1\%$) in the soil and the octanol-water partition coefficient for the solute are known (Karickhoff, 1981; Karickhoff et al., 1979; Means et al., 1980).

How SOM is distributed in aquifer materials greatly effects the sorption kinetics and nonequilibrium behavior of a soil system. The limited insight into the nature and distribution of SOM in soil particles is noted throughout the literature (Young and Ball, 1995; Rebhun et al., 1992; Pedit and Miller, 1994, 1995; Pignatello and Xing, 1996) and evident by the large amount of research being done in this area. Because mass transfer is governed by diffusion of HOCs into micropores and SOM at significant path lengths in the soil, better descriptions of SOM distributions are the logical approach towards improved modeling the behavior. Qualitative observations and estimates of organic carbon fractions of soils are useful as a starting point to describing sorption capacity (Karickhoff, 1981). Ultimately, however, an estimate of the amount, location and type of SOM in a soil particle is needed to model and predict sorption nonequilibrium behavior.

Several researchers provide descriptions of SOM distributions at the grain scale (Pignatello and Xing, 1996; Schwarzenbach et al., 1993; Augustijn, 1993). SOM is envisioned as surface coatings on mineral particles, on micropore walls as thin coatings at variable diffusion path lengths, or as a completely separate particle between minerals. SOM has been described as having a polymer-like structure, wherein long,

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bunched chain molecules create intermolecular voids (Brusseau and Rao, 1989a). Humic substances, the primary constituent of SOM, are believed to exhibit this polymer-like structure. Polymer-like SOM may have either a glassy, inflexible structure or a rubbery flexible structure (Pignatello and Xing, 1996). The latter is consistent with linear isotherms while hysteretic behavior is noted for the glassy polymer model where the rigid structure makes diffusion out of the voids in the polymer more difficult. This concept is consistent with lab observations where temperature increases resulted in glassy polymer samples changing to the rubbery phase and desorbing the solute faster and more completely (Pignatello and Xing, 1996).

Research described by Schwarzenbach et al. (1993) identifies SOM as being largely composed of woody remains of terrestrial plants (humic substances). At the grain scale, SOM composition is believed to be very heterogeneous, further complicating attempts to describe SOM distributions (Pedit and Miller, 1994; 1995). For example, soil from the same sample may often contain SOM of completely different origin resulting in a wide distribution of sorption and desorption rates (Pedit and Miller, 1995). In addition, natural soils typically span a wide range of individual particle sizes and therefore a wide range of diffusion path lengths. Research by Rao et al. (1980a and 1980b), and subsequent work by other researchers, described the effect of particle size on experimental breakthrough curves by showing increased tailing with increased radius.

SOM is about 50% carbon (Schwarzenbach et al., 1993). As such, it is a significant source of sorption, even in small amounts. For this reason, if SOM is present in an appreciable fraction of the soil composition, it is the overwhelming factor governing the sorption of HOCs (Karickhoff, 1981). There is interest in describing the

distribution of SOM within a soil particle because the rate at which equilibrium is achieved is determined by grain-scale geometry.

Two prevalent theories or adaptations thereof, found in the literature are used to describe the diffusion of dissolved chemicals into soil particles and SOM; intraorganic matter diffusion and retarded intraparticle diffusion (Wu and Gschwend, 1986; Brusseau and Rao, 1989a; Ball and Roberts, 1991b; Brusseau et al., 1991; Heyse, 1994; Pignatello and Xing, 1996). Diffusion is a transport process whereby a solute moves through random movement of molecules (Crank, 1975). The magnitude of the molecular motion is determined by the internal energy of the solute molecule, dependent on temperature, and represented by a diffusion coefficient (Szecsody, 1988).

The intraorganic matter diffusion (IOMD) theory attributes slow sorption and desorption of organic compounds to diffusion in a polymer-like flexible matrix (Chiou, 1983; Brusseau and Rao, 1989b; Nkedi-Kizza et al., 1989; Brusseau et al., 1991). This is supported by the nature of SOM, which consists of long chains of organics coiled into tight units to minimize the hydrophobic surface area exposed to the aqueous solution (Schwarzenbach et al., 1993). A sorbing species must diffuse into the pores and voids between the chains to find sorption sites. IOMD is a sorption rate limiting process because of the long and tortuous path some solute molecules must traverse and due to the affinity of the HOCs to the nonpolar moieties of the SOM. This results in molecules taking longer times to diffuse into or out of SOM. The concept of the polymer matrix with deep sorption sites therefore explains nonequilibrium behavior by physical (transport) limitations.

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The physical structure of the solute molecule plays an important role in IOMD and size restriction of some molecules relative to the polymer void spaces is also a possible rate limiting factor. Molecule size and surface area may determine whether a molecule is capable of reaching the deep sites and may complicate the navigation of the molecule into, and out of, the polymer matrix.

Retarded Intraparticle Diffusion (RIPD) is another theory used to explain sorption kinetics. RIPD theory supports SOM distributions in the mineral as the cause of the rate limiting behavior. Sorbate molecular structure and steric hindrances are also factors in RIPD. RIPD is conceptually diffusion into micropores in mineral grains with SOM distributed in and along the micropores (Brusseau et al., 1991). The diffusion paths to the SOM coatings are tortuous but the structure is rigid. Sorption is conceptualized as instantaneous because SOM is believed to exist as thin mono-layers on the mineral surface of pore walls (Ball and Roberts, 1991a; Pignatello and Xing, 1996). Both IOMD and RIPD may exist in a soil particle if SOM fills or blocks a micropore and sorbate must diffuse through the SOM to reach deeper SOM deposits on micropore walls (Augustijn, 1993).

The theories described above (IOMD and RIPD) are used to explain why rate limiting behavior occurs. It is important to note that the theories are not mutually exclusive. Both were developed based on observations made from experiments with different soil types. For soils with low SOM and high microporosity, RIPD may better describe the cause of the rate limited sorption. Conversely, for soils with abundant SOM, IOMD is probably better in describing the nonequilibrium behavior (Augustijn, 1993).

Sorption Models

Conventional methods of modeling sorption include use of equilibrium models, diffusion models, first order approximations of diffusion, or combinations of these approaches. Although equilibrium models cannot simulate sorption nonequilibrium alone, when used in combination with other models such as a diffusion model, the composite or bicontinuum model may better approach reality in soil systems. Such an approach is often used to improve model fits to breakthrough curve data. All of the models assume that partitioning into SOM are the dominant causes of sorption. Rate limitations or sorption nonequilibrium is caused by diffusion into the SOM or soil pores. Lastly, all sorption sites fall along a single sorption path length in a theoretical soil particle. Solute molecules entering a soil pore are assumed to only exit from the same pore when desorbing. Each of these types of models will be reviewed, deficiencies discussed, and improvements proposed. Validation of these models and methods for validation are needed to determine applicability to natural soils.

Diffusion Models

Diffusion models follow Fick's second law and require that particle geometry be known or assumed. Diffusion is either into intraparticle pores or surface diffusion on pore walls (Pedit and Miller, 1994). The mass flux, J, of a diffusing chemical species is described mathematically by Fick's first law (equation (2)):

$$J = -D \frac{\partial C}{\partial x} \tag{2}$$

The contaminant mass flux is directly proportional to the diffusion coefficient, D, and concentration gradient, $\partial C/\partial x$, but in the opposite direction (Crank, 1975).

Although natural soil geometries are heterogeneous and irregular, a uniform spherical shape is often used to approximate all geometries. Fick's second law in spherical coordinates, where r is the particle radius, is given as equation (3):

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right)$$

(3)

In diffusion models, all soil particles are considered to be similar in sorptive properties and geometries. Diffusion models are therefore limited to assuming only homogeneous particles as the diffusion domain. By modifying the diffusion coefficient or the particle radius, the spherical diffusion model can be fitted to breakthrough curve data. Concentration gradients in the particles can be nonlinear which is one reason why diffusion models may do a better job at describing long-term tailing.

Unfortunately, this increased accuracy makes for slow, mathematically complex models because they describe the concentrations at all path lengths in the sphere. The model can be simplified by describing all sorption sites as either in one or two compartments.

Multisite Model: Multiple Sites in Series (MSS)

A finite-difference approach to a diffusion model is used in application of the multiple sorption sites in series (MSS) model. This alternative approach describes the diffusion domain with a frequency distribution of sorption sites along a path length, δ (Heyse, 1994). The size of the sorption compartments are described by this frequency distribution. The function selected for describing the frequency distribution of sorption sites is defined by two parameters. Therefore, the MSS is comparable to other models

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in terms of the number of fitting parameters required. However, the function describing

the sorption sites may be advantageous over the diffusion model because it allows for

simultaneous description of sites near the SOM and liquid interface and sites at long

path lengths. This may be an improvement over modeling particles as spheres. A

conceptual MSS model by Heyse (1994) is presented in figure (1):
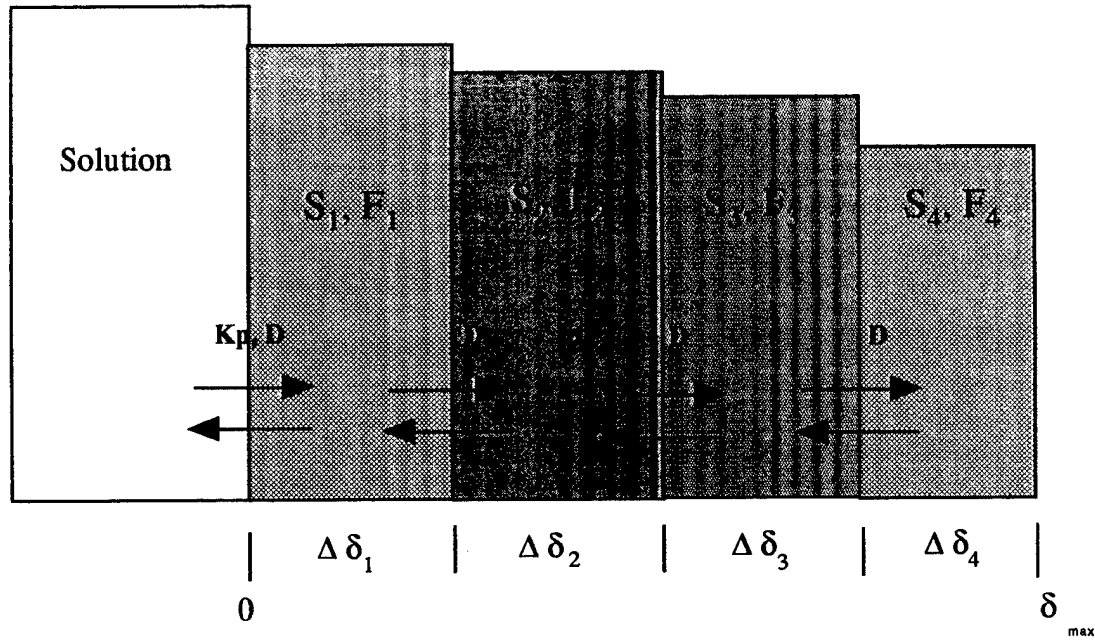
Figure 1.: MSS conceptual model. Sorption site compartments are in series with the aqueous phase

The fraction of sorption sites defined by compartment j sums to one and is described

by equation (4):

$$F_j = \int_{\sum\limits_{j-1} \Delta\delta_j}^{\sum\limits_{j}^{\Delta\delta_j}} f(\delta)\,d\delta \tag{4}$$

Mathematically, the model describes the solute concentration in each

compartment in the sorbed phase. The sorbed concentration rate of change in

compartment j is described by equation (5):

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$$\frac{dS_j}{dt} = -\frac{D_{eff}}{\Delta\delta_j}\left[\frac{S_j - \frac{S_{j-1}F_j}{F_{j-1}}}{0.5(\Delta\delta_j + \Delta\delta_{j-1})}\right] - \frac{D_{eff}}{\Delta\delta_{j+1}}\left[\frac{\frac{F_{j+1}S_j}{F_j} - S_{j+1}}{0.5(\Delta\delta_j + \Delta\delta_{j+1})}\right] \qquad (5)$$

where the total sorbed concentration, S, is the sum of the sorbed concentrations in the j compartments, and where $1 < j < N$. For the first compartment, equation (6) describes the mass transfer:

$$\frac{dS_1}{dt} = -\frac{D_{eff}}{0.5\Delta\delta_1^2}\left[S_1 - K_p C F_1\right] - \frac{D_{eff}}{\Delta\delta_2}\left[\frac{\frac{S_1 F_2}{F_1} - S_2}{0.5(\Delta\delta_1 + \Delta\delta_2)}\right] \qquad (6)$$

For the Nth compartment, equation (7) describes the mass transfer:

$$\frac{dS_N}{dt} = -\frac{D_{eff}}{\Delta\delta_N}\left[\frac{S_N - \frac{S_{N-1}F_N}{F_{N-1}}}{0.5(\Delta\delta_N + \Delta\delta_{N-1})}\right] \qquad (7)$$

The frequency distribution of sorption sites along a diffusion path length in the soil particle is described as equation (8):

$$f(\delta) = \frac{\lambda+1}{\delta_{max}^{\lambda+1}}(\delta_{max} - \delta)^\lambda \quad : \{0 \le \delta \le \delta_{max}\} \qquad (8)$$

Another advantage of the MSS model is the ability to describe diffusion in nonspherical shapes by fitting the lambda shape factor parameter, λ, in equation (8) above. For diffusion in uniform spheres, λ equals two. A uniform coating has λ equal to zero while λ of one describes a cylinder. For SOM, λ is expected to be some value greater than two because SOM consists of a heterogeneous mixture of sizes.

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Like the conventional diffusion model, the MSS model only describes one uniform shape for the particle; all particles are homogeneous. Only one realization of sorption sites can be described for any one path length. Also, only one value for the diffusion coefficient is used in the MSS model; the effective diffusion coefficient, D_{eff}. In reality, the diffusion coefficient varies due to SOM and soil particle heterogeneity. The MSS handles this by describing the sorption sites as a frequency distribution along a path length. Because it is a diffusion model, the MSS is also mathematically rigorous.

First-Order Models

Models approximating diffusion as a first order process have the advantage of being much simpler computationally than a diffusion model. Particle geometries need not be known in lieu of using a first order mass transfer rate to describe the sorption rate process. A first order process means proportionality exists between the difference in sorbed and aqueous phase average concentrations and the mass transfer rate (Young and Ball, 1995). This results in a linear concentration gradient. The number of fitting parameters required to describe the sorption process in the first order model are no more than that required by a diffusion model. The concentration gradient in the soil particles is linear which is a limitation possibly causing failure of first-order models to describe long term tailing.

Continuum of Compartments:

Describing sorption kinetics by including multiple compartments as sorption sites is favorable because this allows for a more detailed description of variation in diffusion coefficients and diffusion path lengths. A first order analytical model which used a

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continuum of compartments approach to sorption kinetics was developed by Connaughton et al, (1993). The distribution of desorption rate constants was described by a continuous gamma function with two fitting parameters. Compartments with very low desorption rate values were important because these sites described the long term tailing observed in nonequilibrium conditions. Using a distribution of rate constants may allow for modeling of soils with a heterogeneous distribution of particle sizes, as is common in natural soils. Because the model is an analytical solution, its use is limited to problems with simple boundary conditions and homogeneous soils.

Multisite Model: Multiple Sites in Parallel (MSP)

The MSP model by Heyse (1994) is based on the Connaughton (1993) analytical model but uses a finite difference solution where a discrete distribution of mass transfer rates defines the size of the sorption compartments. The mass transfer rate is related to the MSS frequency distribution of sorption sites along a diffusion path length by the effective organic matter diffusion coefficient as shown in equation (9):

$$k = \frac{D_{eff}}{0.5\delta^2_{max}}$$

(9)

The simplicity of the MSP model is obvious when comparing the following to the MSS model, equation (5). The MSP model describes the kinetics of the sorbed solute concentration in compartment j as in equation (10):

$$\frac{dS_j}{dt} = k_j\left(F_j K_p C - S_j\right)$$

(10)

Like the MSS model, only two parameters are needed to fit the model to the data. Lastly, the MSP is simple and employs a stochastic method of describing the first order rate constants for the compartments, which probably better suits reality than

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simply modeling sorption with minimal rate constants as is done with one and two-site models.

Because it is a first order model, the MSP also suffers the same disadvantages; all concentration gradients are linear in the soil particles.

Two-Site Model

A two site, first order model is often used for modeling nonequilibrium sorption (Karickhoff and Morris, 1985; Brusseau and Rao, 1989b; Nkedi-Kizza et al. 1989; Van Genuchten and Wagenet, 1989). Observations indicate that overall sorption rates change with time. Initially, the sorption of an organic compound will proceed quite rapidly. Later, slower sorption rates begin to dominate (Karickhoff, 1981; Karickhoff and Morris, 1985; Ball and Roberts, 1991b; Brusseau and Rao, 1989a). The two site model approach divides sorption in two "regions" described by fast and slow mass transfer rates. Conceptually, the two site model is envisioned as in figure (2).
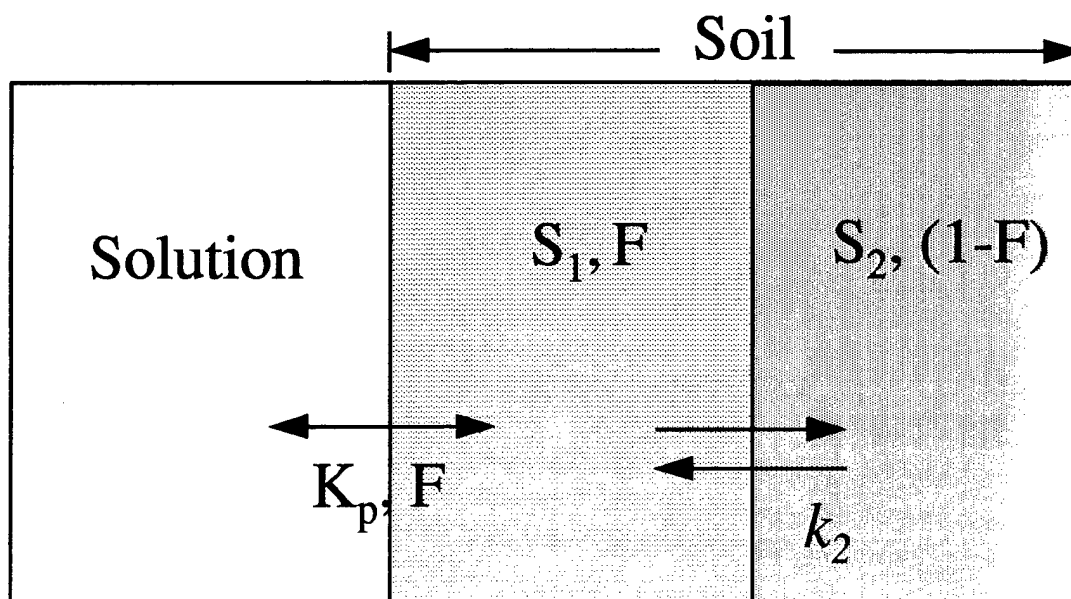
Figure 2.: Two-Site Model

Mathematically, the two site model is described by equations (11) through (13):

$$S = S_1 + S_2 \tag{11}$$

$$S_1 = F K_p C_L \tag{12}$$

$$\frac{dS_2}{dt} = k_2 [K_p C_w (1-F) - S_2] \tag{13}$$

S_1 and S_2 are the sorbed phase concentrations in the fast and slow sites. The sites at equilibrium with the dissolved phase are found near the SOM and solvent interface. Rates used to describe the fast and slow site sorption and desorption are termed k_1 and k_2, respectively. Because K_p can be estimated through batch methods, only the first order rate constant for the S_2 sites and the mass fraction of equilibrium sites, F, are needed for modeling grain-scale mass transfer with a two-site model. These are obtained by fitting the model to experimental data.

Although the two-site model is very simple conceptually and mathematically, it is obviously limited by an inability to describe a wide range of first order rate constants as can be done in the MSP model proposed by Heyse (1994). The first order rate constant, k_2, is also a velocity-dependent parameter.

Justification for Multisite Models

Because partitioning is a diffusion controlled process, a diffusion model was selected as the starting point. Desorption kinetics involving long term tailing may be better described by a frequency distribution of diffusion path lengths, as in the MSS model. This is due to the ability of the MSS to describe geometries other than spherical. This theory will be tested on the MSS model in the experimental work

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described in the following sections. Methods proposed for validation will use synthetic soils, discussed below.

Synthetic Soils

Researchers often use models based on a sphere as the diffusion medium (Young and Ball, 1995; Rao et al. 1980a; Parker and Valocchi, 1986). To truly know the sorptive behavior of a soil/solute interaction, knowledge of the diffusion domain is required. Unfortunately, little is known and probably ever knowable about the geometry of the true soil diffusion domain. Several researchers have used synthetic media to aid in investigating both pore diffusion and organic matter diffusion mass transfer limitations, and their work is reviewed below. The advantage of synthetic media over natural soils is that the geometry of the individual soil particles can be controlled.

Synthetic Media for Pore Diffusion Studies

Rao et al. (1980a) performed early work in use of synthetic aggregates to study relationships of solute sorption and correlation to particle size. This work noted increasing tailing as aggregate size increased supporting the possibility of intraparticle diffusion as the rate limiting process. The investigators studied diffusion in spherical aggregates and development of models to describe the sorption behavior of an experimental system. The properties of the diffusion domain were known so some fitting parameters for the model were given. This allowed for easier validation of the models being investigated.

Skow and Alexander (1992) used the same synthetic media as described by Rao et al. (1980a) to investigate biodegradation kinetics in the presence of spherical aggregates. This study showed that diffusion into the aggregates limited

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biodegradation of contaminants because sorbed phase chemicals are not available to microorganisms.

Synthetic Media for Organic Matter Diffusion Studies

Rebhun et al. (1992) investigated the role of mineral surface adsorption through use of a synthetic aggregate coated with humic acid at varying, but known, amounts. Research by Szecsody (1988) investigating sorption onto sorbent surfaces also recognized the utility of working with particles of known geometry and known SOM distributions as a step towards isolating causes of sorption nonequilibrium.

Paraffin as a Synthetic Media:

Use of a synthetic polymer as a model of SOM has been discussed by Pignatello and Xing, (1996). Selection of a surrogate is difficult because of the heterogeneous nature of SOM itself. However, as a model validation tool, a homogeneous SOM surrogate is preferable because the SOM geometry must be known and sorption characteristics consistent. The sorptive behavior of a heterogeneous SOM model can never be completely described. Therefore, for the purposes of this research, where the goal is to generate data for model validation based on a known diffusion domain, a homogeneous SOM model is advantageous and desired.

Use of paraffin as a synthetic soil has several advantages as candidate for a SOM surrogate (Heyse, 1994). First, paraffin can be easily melted and shaped into desired geometries. Pure grade paraffin is readily available. Purity is important if consistent sorption behavior is to be realized. The presence of other slightly more soluble fractions in the paraffin could effect the equilibrium partition coefficient and the

rate data in sorption experiments. Lastly, paraffin is comprised of long chain hydrocarbon molecules. SOM is believed to consist of very long chain hydrocarbon molecules coiled in tight bunches believed to exhibit a polymer-like structure. Therefore, diffusion into paraffin may resemble diffusion into SOM.

Problems related to use of paraffin were discovered by Heyse (1994). Experimental results indicated an inconsistent equilibrium partition coefficient possibly due to the changing composition of the paraffin media during heating. Equilibrium partition coefficients from 5.03 mL/g to 34.0 mL/g were obtained on the same paraffin media. Heyse (1994) suggested that heating the paraffin to make shapes may have volatilized low molecular weight fractions in the paraffin thus making it more hydrophobic. Also, obtaining the desired geometries (spheres) was not achieved because of the difficulty in molding the molten paraffin. Impurities in the paraffin may present a source of measurement error or interference with analytical laboratory instruments. A strict protocol detailing methods and procedures for making paraffin media must be developed to ensure consistent physical and chemical properties of the paraffin media.

III. DEVELOPMENT OF SYNTHETIC SORBENT

Materials and Methods

Overview of Experimental Approach

Researchers often use batch methods in experiments investigating sorption nonequilibrium. Batch experiments allow for isolation of the diffusion process being studied from effects of advection and dispersion (Pignatello and Xing, 1996; Pedit and Miller 1994, 1995, Karickhoff, 1981). Aliquots are often gently shaken to maintain well-mixed conditions in the solution and data is collected by analyzing samples collected during the course of the sorption experiment. This data is used to show sorption rate relationships and develop sorption isotherms; a constant temperature relationship of the equilibrium aqueous and sorbed phase concentrations in the aliquots. From this relationship is derived the equilibrium partition coefficient (K_p), which is necessary for modeling the diffusion process.

Because solute and soil systems may require long times to reach equilibrium, a sample of the soil being used in the experiments is often pulverized to reduce the equilibration time (Ball and Roberts, 1991b; Pedit and Miller, 1994). Pulverization significantly reduces the diffusion path length to sorption sites and is used as supporting evidence for IOMD and RIPD. If the pulverized soil exhibits faster sorption rates, this is strong evidence of intraparticle diffusion as a rate limiting process.

The following sections discuss materials selected for conducting sorption batch experiments and methods used to perform these experiments. This information includes details on making synthetic media so that follow on research into synthetic soils can reproduce the media and obtain consistent results.

Sorbent, Solute, and Solvents

Paraffin was investigated as a SOM surrogate for use as sorbent in batch experiments. Paraffin was purchased from Aldrich Chemical Supply, lot number 09601KN, CAS number 8002-74-2, and was 99% pure.

Anthracene was selected as the solute used in all sorption experiments. Anthracene is a nonpolar, HOC which because of its low volatility lessens the probability of mass losses due to volatilization. This provides favorable mass balance conditions allowing accurate estimates of sorption rates and an equilibrium partition coefficient. However, because of the very low aqueous solubility, methanol was used as a cosolvent to increase the solubility. Anthracene was procured from Aldrich Chemical Company and was 99% pure. Methanol obtained from Aldrich Chemical Company was of 99.9+% purity and mixed 1:1 in solution with distilled water and used as the solvent in the batch experiments.

Stock solutions for the batch experiments contained trace amounts of anthracene and were prepared by weighing out a known mass of anthracene and adding it to a known volume of the 1:1 MeOH-H_2O mixture. Stock solution was placed in amber, one liter bottles and placed on a stir plate for several days to ensure adequate dissolution of the anthracene. Amber bottles were used as a precaution against possible photodegradation of the anthracene. Stock solution was first filtered using glass fiber filters and a vacuum pump before use in the aliquots. Several bottles of stock solution were prepared in this fashion over the course of the experiments, each with unique solute concentrations, but all less than 1 mg/L. Concentrations were verified using analytical methods described below. The density of the 1:1 stock solution was approximately 0.922 g/ml and was determined by measuring out and

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weighing 1 liter of solution. Laboratory environmental conditions were controlled and maintained at a temperature of approximately 75 °F.

Analytical Techniques

A Hewlett-Packard High Performance Liquid Chromatograph (HPLC) model HP1090 Series L, with a UV lamp and filter photometric detector was used for all sample analyses. The filter was set at 254 nanometers. The UV lamp was warmed up at least one hour before sample analysis. The analytical column was an Alltech Adsorbosphere C18 bonded phase. The column contained 5 micron packing and was 150 millimeters (mm) long with internal diameter of 4.6 mm. The HPLC mobile phase was 100% HPLC grade methanol. Injected sample volumes were 100 microliters based on the volume of the injection loop. The loop was purged with at least five loop volumes from the aliquot being sampled before manual injection. Because part of the loop was submersed in the aliquots during sampling, the loop was cleaned with pure methanol rinse between samples to prevent cross contamination. The mobile phase velocity was maintained at 0.4 ml/minute for all analyses. Oven temperature in the HPLC was set at 32 °C. Sample analysis results from the HPLC are reported as peak areas under a breakthrough curve using the HP model 3390A reporting integrator. Calibration standards for the HPLC were prepared in similar fashion to the stock solution except 100% MeOH was used. Solute concentrations in the standards ranged from 0.0135 to 5.11 mg/L. Additional details on the calibration data is provided in Appendix A.

All weights recorded during the experiments were made using an Ohaus analytical balance.

Equilibrium Partition Coefficient, K_p

The following methods were employed to create sorption isotherms. Bulk unheated paraffin was shredded with a steel screen mesh and aliquots prepared by adding approximately a half gram of the paraffin to preweighed five milliliter (ml), screw-top amber vials with a Teflon septa. About 4-5 mL of stock solution were added to the vials. A small amount of head space was retained in all vials. Initial anthracene concentrations in the vials were 0.17, 0.35, 0.55, and 0.71 mg/L. A similar procedure was followed for aliquots containing shredded paraffin that had been heated for one, two, or three hours at approximately 70 - 100 °C on a heat plate. A replicate was made for each aliquot and a blank sample for each concentration. The blanks contained only stock solution, no paraffin, and would serve to determine concentrations and verify that anthracene did not degrade over the course of the experiment. Two sets of blanks were used for each concentration because the unheated paraffin and the 1, 2, and 3 hour preparations were made on different dates using different preparations of stock solution. One set of blanks was also prepared containing paraffin in anthracene-free 1:1 methanol water solution to confirm no chemical fractions were present in the paraffin wax that would interfere with analysis of the anthracene. Appendix A summarizes the information on aliquots prepared and analyzed for determination of K_p. Because no mass leaves the batch system, the total mass of anthracene in an aliquot remains unchanged. Initially, the paraffin contains no sorbed anthracene ($C_{s_i} = 0$). The final sorbed phase concentration is determined by mass balance, equation (14) (Heyse, 1994):

$$C_{s_f} = \frac{V_{w_i}(C_{w_i} - C_{w_f})}{M_s} \qquad (14)$$

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A sorption rate experiment was performed to determine the time necessary for shredded paraffin aliquots to reach equilibrium. Results supported sampling times selected for analysis of the aliquots. Figure 3 shows sample analysis results for aliquots used for determination of K_p. Two additional aliquots were sampled at earlier times to define the sorption rate curve for the shredded paraffin but these were not used in calculating the average K_p as these aliquots were not at equilibrium. Two other aliquots were sampled at longer times for comparison to those sampled at 13-18 days. Appendix A contains the individual sorption isotherms for each of the heated and the unheated paraffin preparations.
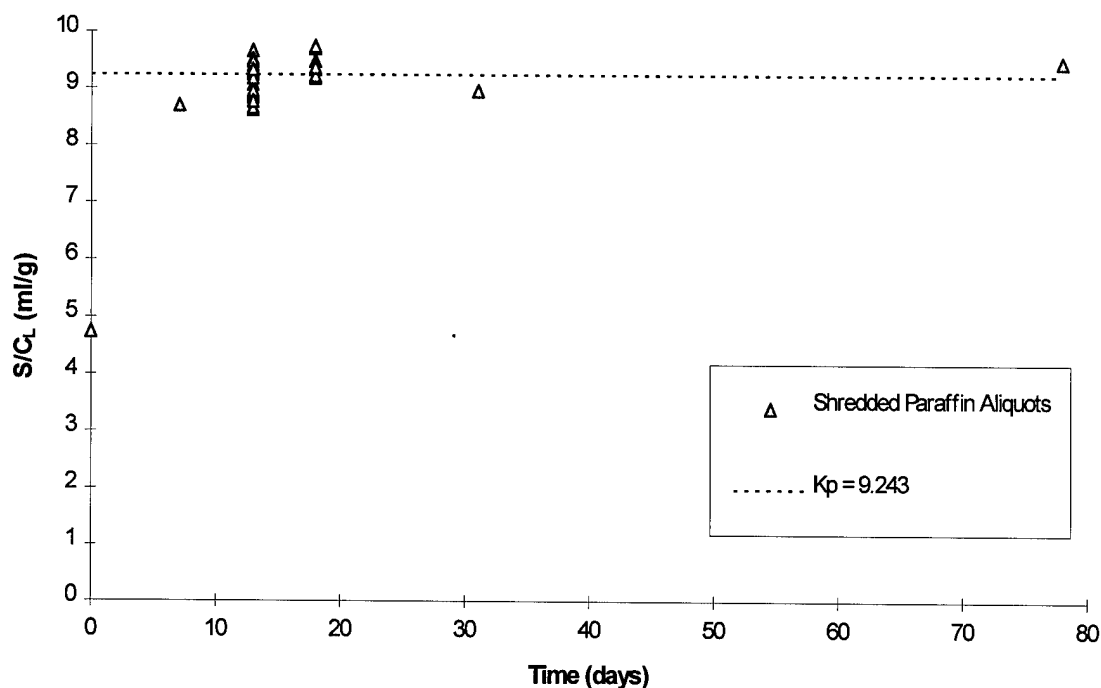
Figure   : Graph of shredded paraffin aliquots sampled at 1 hr, 7 days, 13 days, 18 days, 30 days, and 78 days after preparation.

Aliquots for K_p determination were allowed to equilibrate for up to eighteen days. A sample of the solution in the aliquots was removed and analyzed using the HPLC. Aliquots were only used for one sample each. The maximum solute concentration used

was less than one half the solubility in the MeOH-H$_2$O solution so that a linear sorption isotherm would result. This estimate is a common rule of thumb used to ensure linear sorption isotherms. Figure 4 shows the resulting linear sorption isotherm based on all of the heated and unheated paraffin preparations equilibrated for 13 to 18 days:
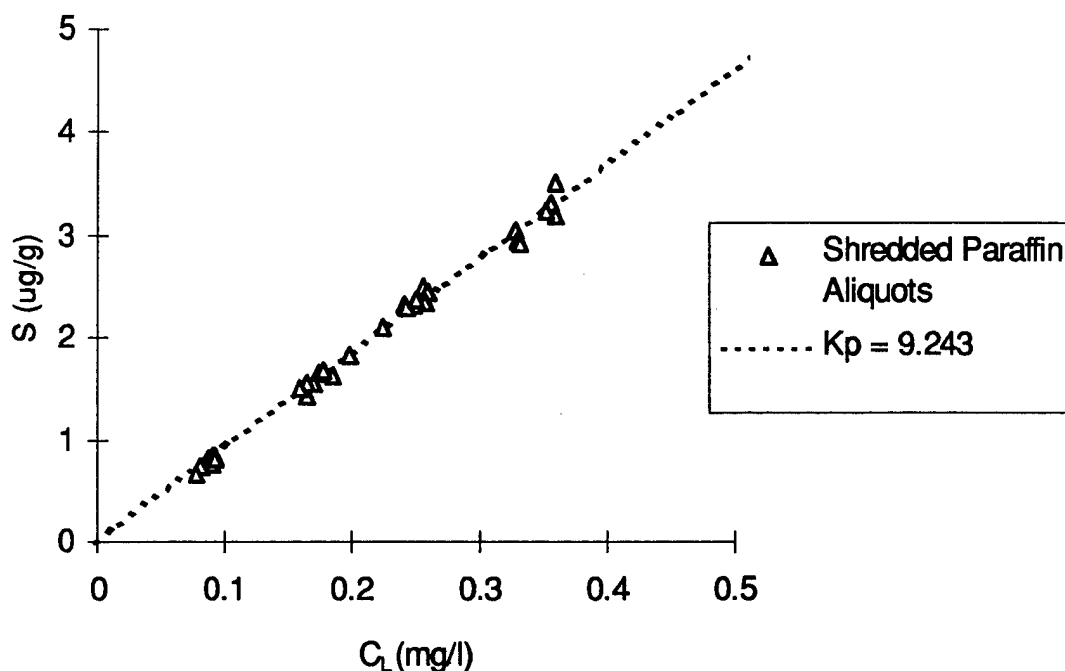
Figure 4.: Sorption Isotherm for heated and unheated paraffin equilibrated for 13-18 days with anthracene in 1:1 methanol-water solution

K$_p$ for each aliquot was calculated using equations (1) and (14).

Results:

This experiment determined that heating the paraffin did not change the equilibrium partition coefficient. Consistent values for K$_p$ were obtained among the batches and may be attributed to the purity of the paraffin used in the experiment. The average value for K$_p$ is 9.24 mL/g. This value was used for model validation experiments. Qualitatively, Figure 4 and Figure 5 show strong support that the K$_p$ is the same regardless of heating time. A statistical analysis on the individual K$_p$ values and experiment wide estimate was performed. A one-way analysis of variance (ANOVA)

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on the K_p values for each of the four sets of aliquots distinguished by heating times revealed that three of the four sets of aliquots had the same mean K_p with 95% confidence. The remaining set (the 1 hour samples) had the same mean K_p with 95% confidence as one other set. Figure 5 shows the individual K_p results grouped by heating times:
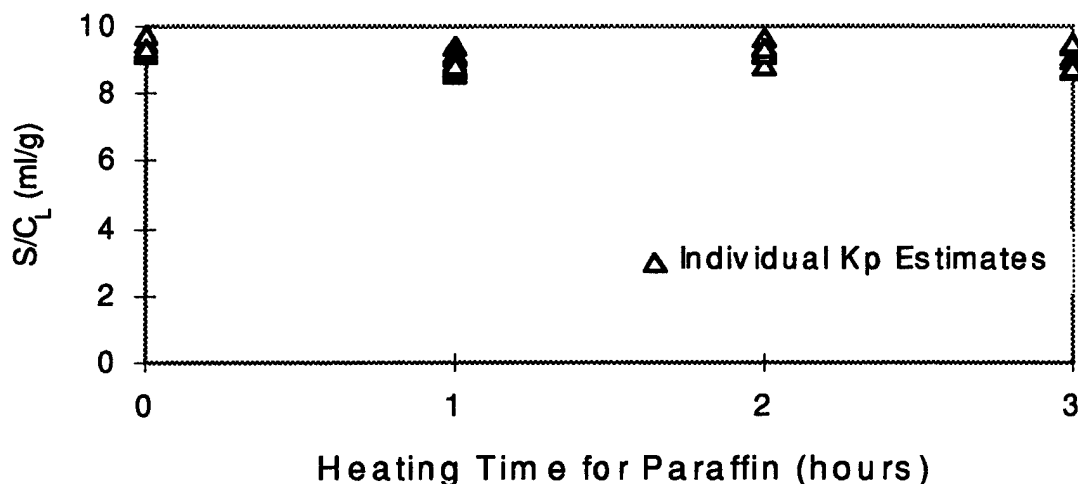
Figure 5.: K_p estimates of individual aliquots

The ANOVA results are presented in Appendix A along with all individual sorption isotherms.

Protocol Development

Several paraffin geometries were produced for use in batch sorption experiments. Different uniform sizes and shapes were needed so that the MSS model could be tested. Three sphere sizes were selected for investigating partitioning based on Fickian diffusion (Crank, 1975; Rao et al. 1980a, 1980b). Also, a uniform geometry (a thin coating) was selected to obtain data for shapes other than spherical and eventual testing of the MSS model.

Initially, a mold was considered the best method for making the desired shapes. This would allow pouring of molten paraffin and cooling to the exact geometry desired. Several molds were made from various materials to produce paraffin spheres. Experiments in pouring the molten wax and shaping the paraffin failed to produce promising results due largely to the thermal expansion of paraffin. When cooled to solid state, the paraffin experienced a significant volumetric reduction leading to misshapen, inconsistent, and undesirable geometries.

Eventually, hand rolling of the paraffin wax was used to make the required shapes. Paraffin was slowly heated and melted then a small amount was dropped onto aluminum foil and subsequently hand-rolled. Hand rolling did not produce a perfect sphere. A thin gauge stainless steel template was made through which were drilled three holes of different diameters: 0.234, 0.196, and 0.157 inches (approximately 6, 5, and 4 mm, respectively). These sizes were arbitrarily selected although dexterity limitations prevented making spheres any smaller than the smallest size noted. Unfinished, rolled spheres were turned through the various diameter holes in a process similar to lathing. Spheres were placed in separate vials according to size. This process produced spheres of consistent roundness, diameter, and mass. Table 1 is a summary of statistics on several batches of spheres made this way.

Figures 6 through 8 show the respective probability plots for the sphere masses and show that masses are normally distributed for each size sphere.

Table 1: Statistics on Manufactured Paraffin Spheres

Sphere Size	Dia (in.)	# Tested	mass (g)	Avg. Mass (g)
Large	0.234	190	17.5988	0.0926
Medium	0.196	137	7.5601	0.0552
Small	0.157	224	6.3127	0.0282

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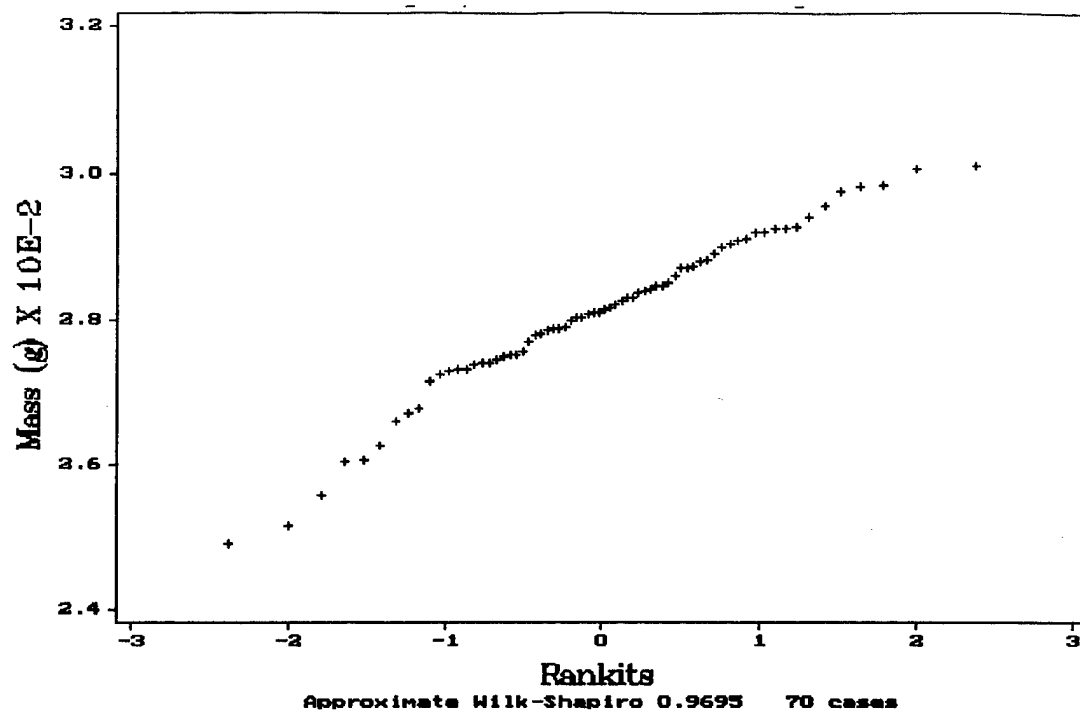
Figure 6.: Normal probability plot for small paraffin spheres
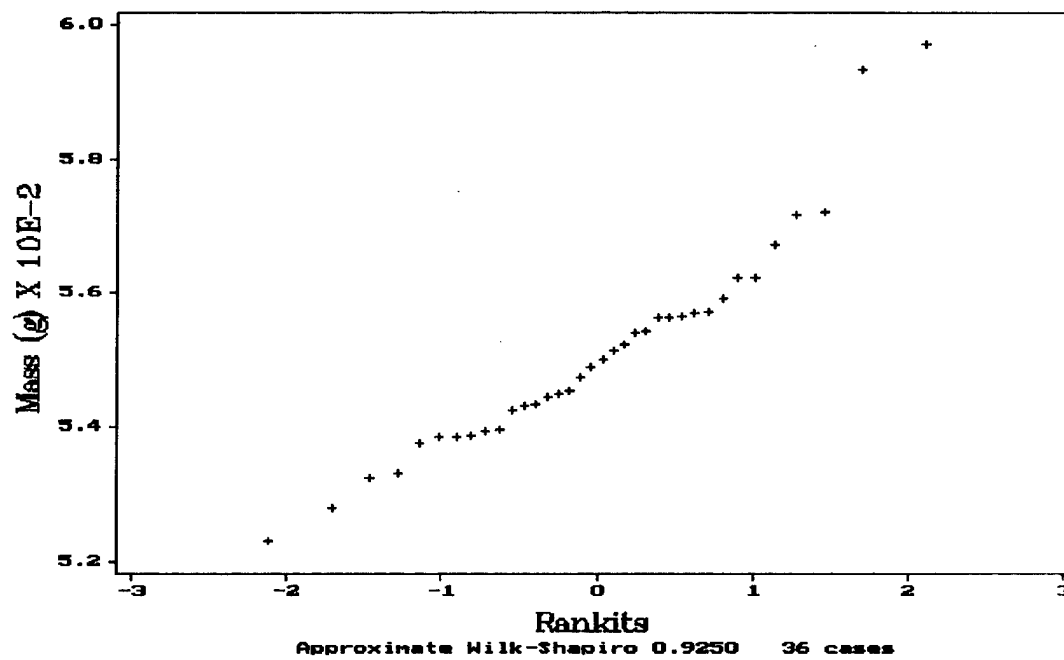
Figure 7.: Normal probability plot for medium spheres
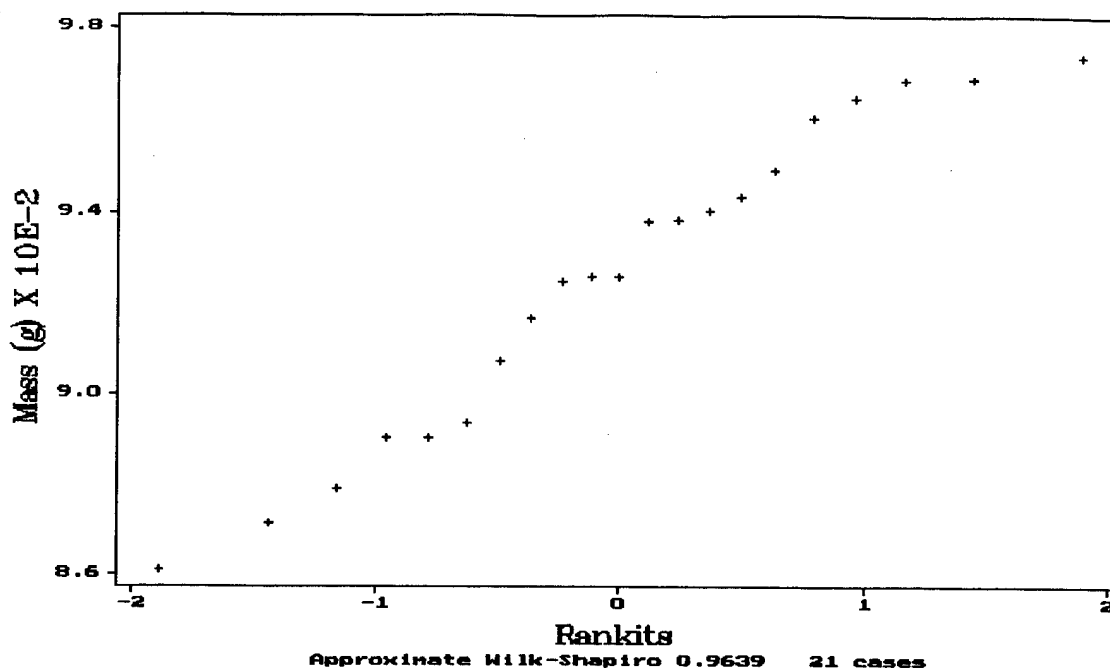
Figure 8. Normal probability plot for large spheres

Table 2 provides further statistical data on the spheres tested:

Table 2: Statistical Summary of Spheres

Statistical Summary	Sphere Size		
	Large	Medium	Small
Mean	0.09253	0.05511	0.02808
Standard Deviation	0.00342	0.00158	0.00110
Minimum	0.0861	0.05232	0.02491
Maximum	0.0974	0.05972	0.0301
Count	21	36	70

Later, spheres were made by pouring molten paraffin into an open ended plastic mold producing small cylinders with an oversized diameter and length. Using a dowel rod, cylinders were extracted from the mold after cooling, but while the paraffin was still soft and malleable for shaping. These were shaped using the template discussed above. This process was faster than hand rolling and produced well-shaped spheres exhibiting the desired qualities.

Thin paraffin coatings (a plane sheet model) were made by twice dipping 4mm glass balls into molten paraffin using small forceps. The cooler temperature of the

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glass ball resulted in a film of paraffin adhering to the ball surface upon removal. The ball was lathed or turned in the medium size template hole (0.196 in) so that the paraffin coating was kept as uniform and centered as possible, and resulted in a coating of approximately 0.5mm thickness. Earlier experiments with a thicker coating produced inconsistent, variable results believed to be caused by nonuniform coatings.

Appendix B contains a stepwise protocol outlining the manufacture of the paraffin spheres and coatings. All experiments used spheres and coatings prepared in this fashion.

IV. MODEL VALIDATION

The purpose of this part of the research was to determine if the MSS model could predict the observed results from batch sorption studies using the paraffin media described above. The ability of the model to simulate the correct rate data and predict the known values of the model parameters that described the distribution of sorption sites was tested and used as a means to determine validity of model assumptions.

Batch Studies to Obtain Data for Model Fitting and Validation

Aliquots were prepared in similar fashion to those used in determination of K_p for the anthracene in the paraffin and MeOH-H_2O system. The batch reactor consisted of either a 40 ml or 5 ml amber screw top vial with Teflon septa. The initial solution concentration was the same for all aliquots within an experiment but different between some experiments because of different stock solutions used. All aliquots were identified by the size of the paraffin sphere and/or the uniform geometry. One set of aliquots was prepared for each sphere size. Another set was made for coatings only. Two sets of aliquots were prepared using mixed (but known) sizes of paraffin spheres. Finally, a set was prepared using mixed sizes of spheres and several coated glass balls. Aliquots were prepared by first placing the paraffin spheres in a preweighed vial, weighing the vial, then filling the vial with stock solution and reweighing.

After preparation of aliquots, vials were placed on a shaker table for gentle agitation and periodically removed for sampling to determine concentrations of anthracene remaining in solution. Sample times were selected to ensure adequate definition of the sorption rate curve at short times and long enough to ensure aliquots were at or near equilibrium. Samples were directly injected into the HPLC from the

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aliquot. Aliquot weights were recorded before and after sampling so data could be maintained on boundary conditions for the batch experiments. This allowed determination of the anthracene sorption rate into the paraffin media. Multiple experiments were performed to demonstrate that media could be made consistently and give reproducible results. Appendix C contains data on aliquot sample analysis results including concentrations in solution and in the sorbent at sampling times, and volumes removed during sampling. Table 3 is a summary of the aliquots prepared with large (Lg), medium (Med), small (Sm), and paraffin coated glass (G) spheres. As in the K_p determination experiments, replicates and blanks were prepared. Blanks were used to verify both initial conditions and purity of the paraffin. Also, a blank and replicate containing uncoated glass balls in stock solution was used to verify no sorption was taking place on the glass surface or through diffusion into the glass. Aliquots containing crushed paraffin spheres were prepared and analyzed concurrent with the last round of sampling to serve as a comparison with final K_p estimates. Controls and initial conditions were used to ensure HPLC operation was consistent. Analysis results of initial conditions are presented in Appendix A and show that HPLC performance over the course of the experiments was consistent.

The initial condition replicates were analyzed concurrent with the last sample to indicate if anthracene degraded over the course of the experiment. Results for all blanks analyzed, and the initial condition replicates sampled and analyzed during the last sample round are presented in Appendix C. For the remainder of the discussion, all experiments and results will be referred to by the aliquot designator in Table 3.

Table 3: Summary of Aliquots Prepared for Sorption Studies

| Aliquot | # of Spheres | | | | Mass (g) | | Initial Vol Solv. (mL) | Initial Solv.Conc (mg/L) |
	Lg	Med	Sm	G	Paraffin	Solvent (initial)		
1B	22	-	-	-	2.0383	18.5811	20.1530	0.7139
2B	22	-	-	-	2.0246	18.3382	19.8895	0.7139
3B	6	-	-	-	0.5666	3.9459	4.2797	0.8113
4B	6	-	-	-	0.5622	3.8205	4.1437	0.8113
6B	6	-	-	-	0.5794	3.9532	4.2876	0.8113
1M	-	36	-	-	1.9841	17.4415	18.9170	0.7139
2M	-	36	-	-	1.9949	18.6873	20.2682	0.7139
3M	-	9	-	-	0.5054	3.9551	4.2897	0.8113
4M	-	9	-	-	0.5062	3.8853	4.2140	0.8113
6M	-	9	-	-	0.5120	4.0102	4.3495	0.8113
1S	-	-	71	-	1.9927	18.4908	20.0551	0.7139
2S	-	-	71	-	2.0018	18.6127	20.1874	0.7139
3S	-	-	18	-	0.4823	4.0801	4.4253	0.8113
4S	-	-	18	-	0.5008	3.9904	4.3280	0.8113
6S	-	-	18	-	0.5087	3.9387	4.2719	0.8113
1BM	11	18	-	-	2.0154	18.3699	19.9240	0.7139
2BM	11	18	-	-	2.0297	18.3712	19.9253	0.7139
3BM	3	4	-	-	0.5231	3.9139	4.2450	0.8113
4BM	3	4	-	-	0.5193	3.9415	4.2749	0.8113
6BM	3	4	-	-	0.5141	4.0476	4.3900	0.8113
1ALL	7	12	24	-	2.0050	18.4702	20.0328	0.7139
2ALL	7	12	24	-	1.9745	23.5680	25.5618	0.7139
3ALL	2	4	4	-	0.5199	3.9373	4.2704	0.8113
4ALL	2	4	4	-	0.5230	3.9340	4.2668	0.8113
6ALL	2	4	4	-	0.5256	3.9300	4.2625	0.8113
1MIXB	10	7	6	10	1.7209	12.3377	13.3815	0.7139
2MIXB	10	7	6	10	1.6725	12.6714	13.7434	0.7139
3MIX	2	2	2	3	0.4305	3.9388	4.2720	0.8113
4MIX	2	2	2	3	0.4244	3.8767	4.2047	0.8113
6MIX	2	2	2	3	0.4331	3.9265	4.2587	0.8113
1GB	-	-	-	30	0.6293	10.9499	11.8762	0.7139
2GB	-	-	-	30	0.6319	10.8403	11.7574	0.7139
7G	-	-	-	9	0.2053	4.0627	4.4064	0.8113
8G	-	-	-	9	0.2189	3.9964	4.3345	0.8113

Equations:

Boundary conditions change during the sorption rate experiments because some solution volume was periodically removed from the aliquots for analysis. The volume removed is accounted for in the mass balance equation, using equation (15):

$$S_n = \frac{(C_{L_i} V_{L_i} - \sum_{j=1}^{n-1} C_{L_j} V_{R_j} - C_{L_n} V_{L_n})}{M_s} \quad (15)$$

Results

Reproducibility of sorption rate data was obtained between experiments using the paraffin spheres and coatings. Figure 9 is an example of the types of plots obtained for most of the experiments and shows the reproducibility of rate. Additional plots are presented in Appendix C.
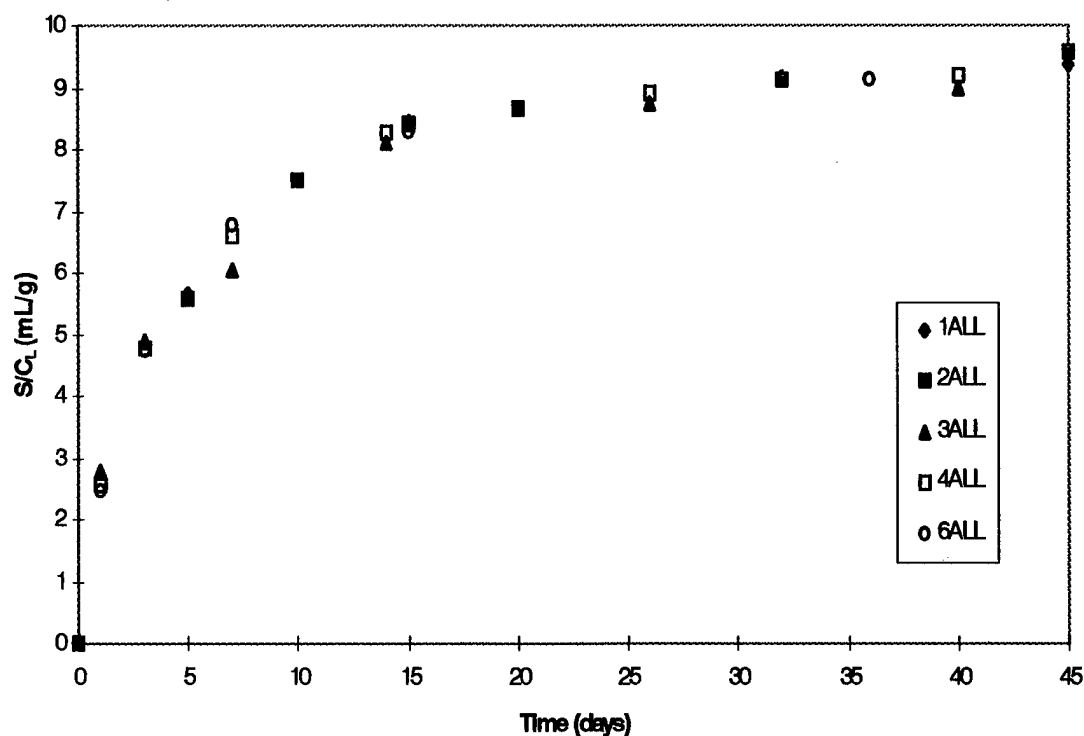
Figure 9: Rate data on aliquots containing all sizes of spheres

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Statistical analysis of the K_p values for aliquots containing paraffin spheres

shows that mean K_p between all experiments (9.265 mL/g) agrees with the K_p value

estimated using shredded paraffin (9.243 mL/g). Comparison between experiments

showed that the mean K_p values in the 5 ml vials were the same with 95% confidence.

Experiments with aliquots in the 40 ml vials averaged a slightly higher K_p than did 5 ml

aliquots. However, as can be seen qualitatively with the rate data plots and eventual

equilibrium points, results are very consistent and virtually indistinguishable. The

ANOVA table and summary statistics for the K_p estimates for experiments containing

paraffin spheres are presented in the tables below:

Table 4: ANOVA for Experiments 1,2,3,4 and 6
```
STATISTIX 4.1
ONE-WAY AOV FOR: NO12 NO34 NO6
```

SOURCE	DF	SS	MS	F	P
BETWEEN	2	0.58086	0.29043	15.63	0.0001
WITHIN	22	0.40892	0.01859		
TOTAL	24	0.98978			

VARIABLE	MEAN	SAMPLE SIZE	GROUP STD DEV
NO12	9.4502	10	0.1527
NO34	9.1257	10	0.1317
NO6	9.1716	5	0.1035
TOTAL	9.2647	25	0.1363

Table 5: Tukey Analysis on the Means for Experiments 1,2,3,4, and 6
```
STATISTIX 4.1
TUKEY (HSD) PAIRWISE COMPARISONS OF MEANS
```

VARIABLE	MEAN	HOMOGENEOUS GROUPS
NO12	9.4502	I
NO6	9.1716	.. I
NO34	9.1257	.. I

```
THERE ARE 2 GROUPS IN WHICH THE MEANS ARE NOT SIGNIFICANTLY
DIFFERENT FROM ONE ANOTHER.  REJECTION LEVEL 0.050.  STANDARD
ERRORS VARY BETWEEN COMPARISONS BECAUSE OF UNEQUAL SAMPLE SIZES.
```

Table 6: Summary Statistics on K_p

Kp for Exp 1,2,3,4,6	
Mean	9.2619
Standard Deviation	0.2169
Minimum	8.9241
Maximum	9.6709

Final K_p estimates for each experiment are in Appendix C, Table C-2, including estimates of sorbed phase to aqueous phase concentration at the respective sampling times.

These experiments achieved two goals:

1. Demonstrate that consistent, reproducible results are possible using the paraffin synthetic soil.

2. Develop rate data for testing the MSS model.

MSS Model Validation

Model Parameter Estimates

Experiments with uniform spheres have two of the required fitting parameters for the MSS model defined: the maximum diffusion path length, δ_{max}, equal to the sphere radius, and the shape factor, λ, equal to two. The partition coefficient was also known from the shredded paraffin experiments. and set to a constant in all of the model input files. The effective diffusion coefficient, D_{eff}, was then determined by fitting the MSS model to the rate data. The average value of D_{eff} was determined and then fixed to a constant in the input files for all remaining aliquots. The true interest of this study was to determine if the vials containing the mixture of sizes and shapes can be adequately described by the fitting procedure in the MSS model. An approximation of

the real frequency distribution of sorption sites along a path length can be determined using equation (8) for the ALL aliquots because the geometry and mass fractions of sizes are known. Distribution of individual sizes were weighted by their mass fraction in any aliquot. By adding the mass fraction contribution of each sphere size in a respective aliquot, a composite, real distribution of sites is developed as in Figure 10. The remaining real distributions for all aliquots are presented in the following sections or in Appendix D. The test of the model is to determine if the real composite distributions can be predicted by using the rate data obtained in the experiments. The shape parameters for real soils are unknown so the model must be able to demonstrate this ability without fixing the known parameters.
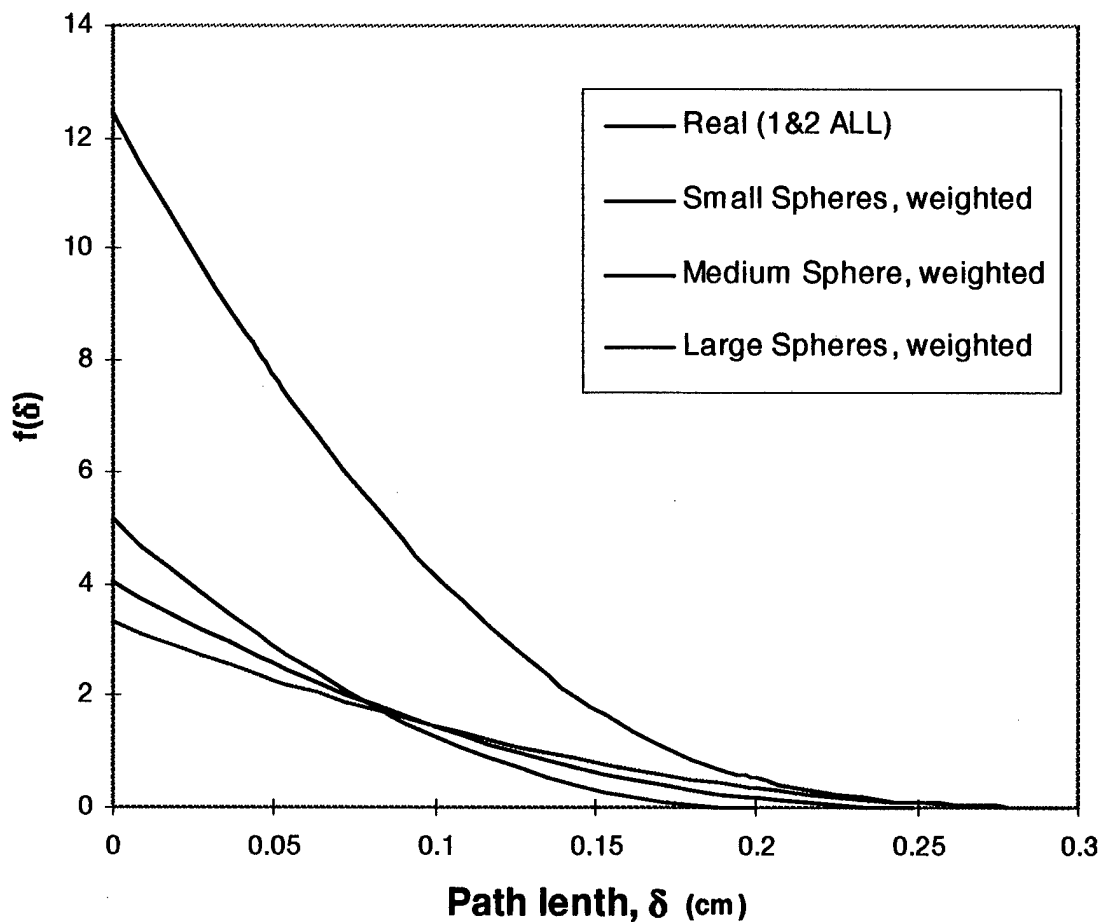
Figure 10: Composite real distribution of sorption sites for 1&2 ALL aliquots

A computer numerical model of the MSS written by Heyse (1994) in FORTRAN programming language was used to generate predicted rate data and used a fitting model (TESTFIT, written by Meeter and Wolfe, 1968) to fit parameters needed to solve for the frequency distribution of sorption sites (equation (8)). The MSS model predictions were compared to predictions of an analytical model by Crank (1975) and shown to provide the same solution. Using initial estimates of the fitting parameters, and rate data and boundary conditions from the batch experiments, the model performs a multiple regression on the data, minimizing the sum of squares for error (SSE), and solves for the parameter values that best fit the data using equation (8). The optimum result is for the model to converge on values for the fitted parameters that are the known reality (fitted sorption site distribution matches the real sorption site distribution). The model was tested by fitting either one or two parameters. One parameter fits were first performed on D_{eff} for aliquots with only uniform sizes. These results were averaged and the average D_{eff} used as input for aliquots containing mixed sizes and shapes, which were in turn fitted for δ_{max} and λ. In reality, at least two parameters will always have to be fitted for a real soil, so the model's ability to perform in this capacity was an important step. Model results for D_{eff}, δ_{max}, and λ were recorded, analyzed statistically, and used to generate graphical output for qualitative comparison with known real distributions.

Following the one and two parameter fits, predicted rate data was obtained from the MSS model and compared with the real rate data from the experiments containing mixed sizes of spheres and coatings. These results are presented graphically below for aliquot 1BM in Figure 11. The MSS predicted rates agree very well with the

observed rate data from the batch experiments. This was the case for all MSS fits performed on aliquot rate data.
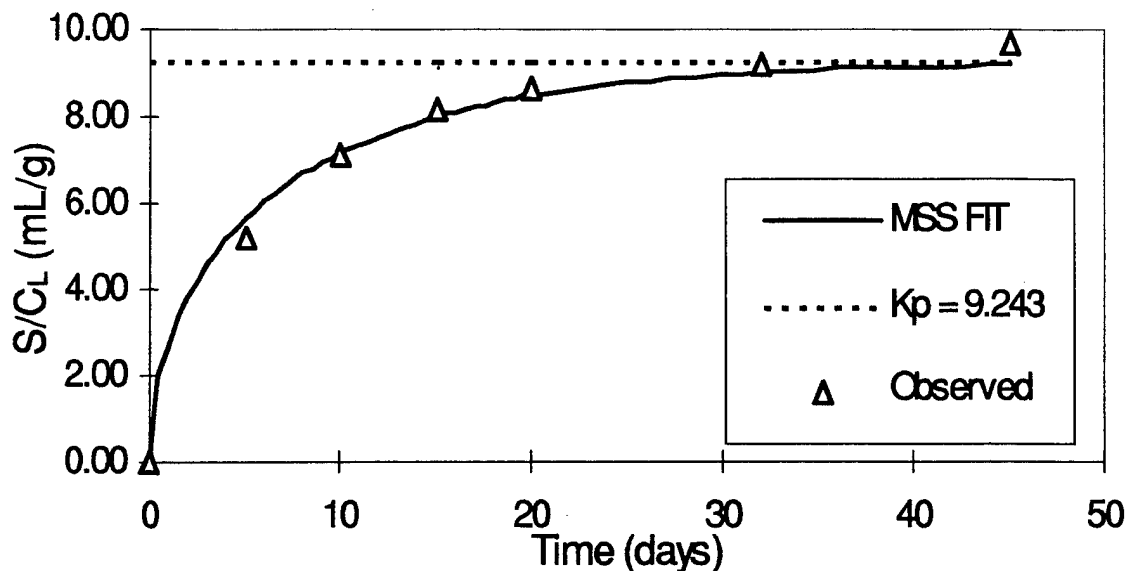
Figure 11: MSS fit of rate data

While matching the true rate data is an important test for the model, it does not prove model validity but only an ability for curve fitting. The true validation is accurate prediction of the sorption site distributions. After the rate data was accurately fitted, additional one and two parameter fits were performed simultaneously for multiple experiments. The purpose of running simulations with multi-experiment data was to observe the model behavior using rate data from more than one experiment. These results are also presented graphically in the next section and in Appendix D

Results

D_{eff}: Analysis of the uniform size aliquots resulted in an estimated average value for D_{eff} of 6.43 x 10^{-9}. Two aliquots, both from the same experiment, were discarded from this average based on analysis of the plot of the D_{eff} values for

individual sizes with 95% confidence intervals, shown as error bars (figure (12)). The mean is outside the confidence interval for these two aliquots. This is further discussed in the following sections describing simulations where D_{eff} was varied between maximum and minimum values reported to see the influence on the shape of the frequency distributions.
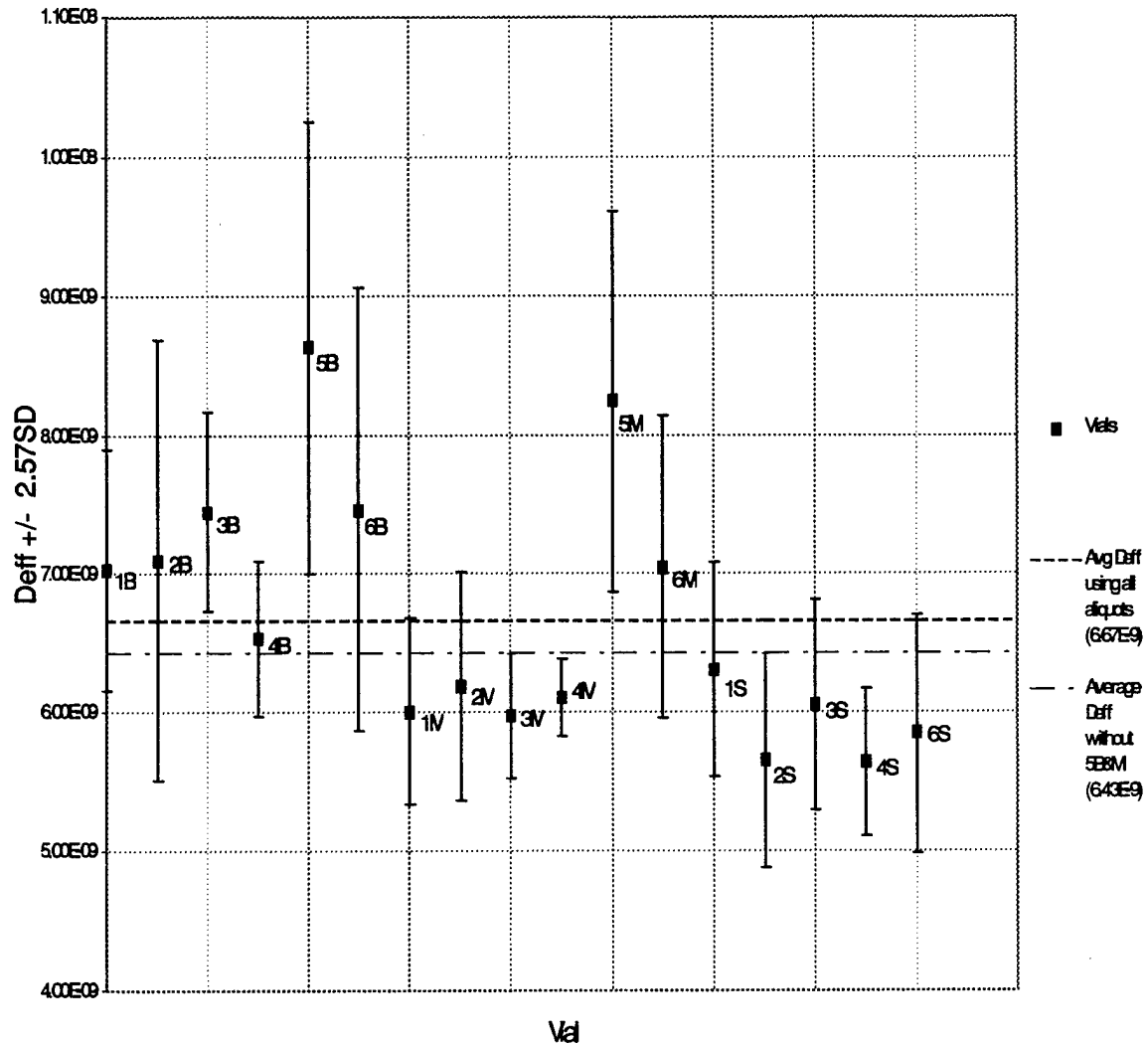
Figure 12: Fitted D_{eff} for individual uniform size aliquots

MSS model results for fitting D_{eff} on aliquots containing only uniform sizes are summarized in Table 7.

Table 7: Summary of Fitted Deff

EXP #	SPHERE SIZE		
	LARGE	MED	SMALL
1	7.04E-09	6.01E-09	6.31E-09
2	7.1E-09	6.19E-09	5.66E-09
3	7.45E-09	5.97E-09	6.06E-09
4	6.54E-09	6.11E-09	5.64E-09
6	7.46E-09	7.05E-09	5.85E-09

Statistical Analysis on the results also revealed that the average D_{eff} based on sphere size was not the same at 95% confidence for all sizes. Results for the large size spheres had a higher mean D_{eff} than the small and medium sizes at a 0.05 significance level as shown by the p-value in Table 8 and Table 9. The mean for these latter sizes was found to be statistically the same at this significance level as shown in Table 10.

The three ANOVA statistical investigations on D_{eff} are summarized below:

Table 8: ANOVA on D_{eff} for Aliquots with Uniform Size Spheres

Anova: Single Factor (Significance Level = 0.05)						
SUMMARY						
Groups	Count	Sum	Average	Variance		
LARGE	5	3.56E-08	7.119E-09	1.43E-19		
MED	5	3.13E-08	6.267E-09	2E-19		
SMALL	5	2.95E-08	5.903E-09	8.05E-20		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.89E-18	2	1.945E-18	13.77938	0.000779	3.88529
Within Groups	1.69E-18	12	1.412E-19			
						REJECT !!
Total	5.58E-18	14				

Table 9 ANOVA on D_{eff} for Large and Medium Uniform Size Spheres

Anova: Single Factor (Significance Level = 0.05)						
SUMMARY						
Groups	Count	Sum	Average	Variance		
LARGE	5	3.56E-08	7.119E-09	1.43E-19		
MED	5	3.13E-08	6.267E-09	2E-19		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.81E-18	1	1.811E-18	10.56153	0.011704	5.317645
Within Groups	1.37E-18	8	1.715E-19			
Total	3.18E-18	9				REJECT !!

Table 10: ANOVA on D_{eff} for Medium and Small Uniform Size Spheres

Anova: Single Factor (Significance Level = 0.05)						
SUMMARY						
Groups	Count	Sum	Average	Variance		
MED	5	3.13E-08	6.267E-09	2E-19		
SMALL	5	2.95E-08	5.903E-09	8.05E-20		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.32E-19	1	3.317E-19	2.364823	0.162656	5.317645
Within Groups	1.12E-18	8	1.403E-19			
Total	1.45E-18	9				DO NOT REJECT !!

The apparent dependence of diffusion coefficient on sphere size was investigated. Larger D_{eff} values typically mean a faster approach to equilibrium. Despite the greater average D_{eff} for the large spheres, this is not the case. Larger particle sizes mean greater diffusion path lengths for deep, internal sorption sites and so slower sorption. These slower sorption rates for the large spheres are shown graphically below in Figure 13. Using results from experiment 2 as an example, the small and medium spheres have visibly higher S/C_L values early in the sorption experiment.
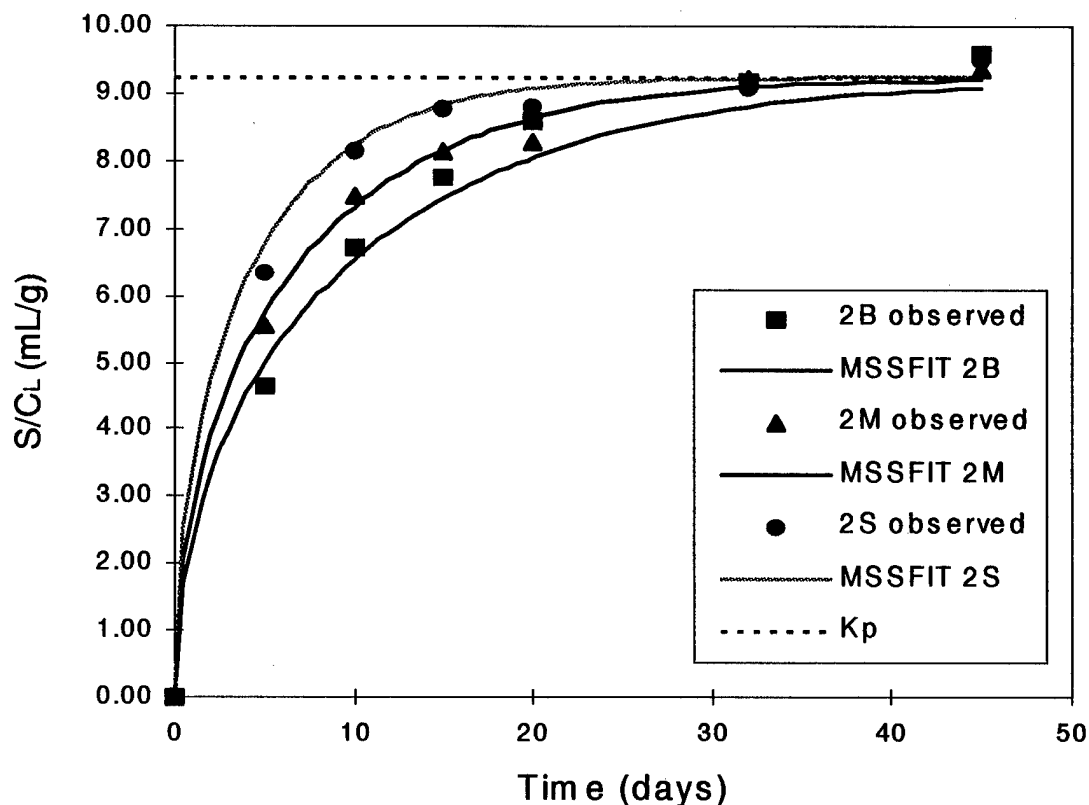
Figure 13: Rate data from experiment 2

One possible explanation for this seemingly conflicting result for D_{eff} and the sorption rate may be the relationship of surface area of spheres and surface or film diffusion. The presence of a thin film of poorly mixed solution around the exterior of each particle can limit mass transfer. Because the solution in this case is most likely well mixed, film diffusion can probably be ignored. Aliquots with small spheres have the most surface area exposed for sorption to occur and so surface diffusion effects would tend to decrease D_{eff} the most for these aliquots. This need not impact the description of the sorption rate. For the small spheres, the exterior sites are responsible for characterizing the overall sorption process. For this reason, sorption rates are initially considerably faster for the small spheres as shown graphically. Conversely, aliquots with large spheres have less exposed surface area and so fewer

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sorption sites near the sorbent/solution interface. Therefore, rates are predictably slower. This however does not explain why D_{eff} is larger when the sorbent material is identical.

Another possibility may involve an increased tortuosity factor for increased particle size. Equation (16) describes the effective diffusion coefficient:

$$D_{eff} = \frac{\phi \, T \, D_0}{K_d^*(1-\phi)\rho_s + \phi}$$ (16)

Assuming the paraffin density and porosity are constant, and K_d^* and D_0 are independent of particle size, the tortuosity factor, T, remains the only variable which may impact the D_{eff} result. Therefore, the possibility that the tortuosity factor increases with increasing particle size is perhaps one explanation of the increased D_{eff} result for the large spheres. This could be a result of methodology used in preparing the paraffin spheres that altered the tortuosity of the sphere near the surface, such as with using the template for turning the spheres. Unfortunately, a belief that the tortuosity factor caused the differing D_{eff} values cannot be proved with the data obtained here and so this is merely speculative.

Two other possibilities will be discussed together as they pertain to the methods used to manufacture the paraffin spheres and the aliquots. Entrapped air in the paraffin spheres may have been a diffusion limiting factor. Air must be forced out and replaced by the solution in the aliquot for the anthracene to diffuse to the sorption sites. However, if this was a possible cause, the results would probably be most affected for the spheres containing the longest diffusion path length. Therefore, the results for the large spheres would be expected to be significantly different, as they are, however, the magnitude of D_{eff} would be lower because diffusion would be limited. This is not the

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case here so entrapped air is probably not a possible cause. Using hand rolling as was done for experiment 1&2 versus a mold, as was done for experiment 3&4, also may have entrapped more air in the spheres initially. This does not seem to be the case however, because the results for D_{eff} are very consistent between sizes of these batches. To disprove entrapped air, or the presence of air in the intermolecular spaces of the paraffin as a possible limiting factor, future experiments could be modified by first immersing the paraffin spheres in clean 1:1 $MeOH$-H_2O for several days and allowing displacement of any air. Pre-soaking the spheres may also indicate if swelling of the paraffin is somehow causing a diffusion limitation and inconsistent behavior among sphere sizes, although this seems unlikely.

The other possibility regarding experimental methods may be due to some impurity on the surface of the paraffin spheres as a result of hand rolling them and turning them through the sizing template. Most possibly this would be a film of oils from the fingers during the smoothing and shaping process. Although this seems unlikely, it also cannot be ruled out. If a film of oil from the skin was present, this may cause results from the smaller spheres to have lower D_{eff} values because aliquots with these sizes have the most exposed surface area. Unfortunately, making the spheres with latex gloves was too cumbersome and limited dexterity. Presoaking the spheres may also rule out this cause as a possibility.

The cause of the variable D_{eff} values among sizes is either a result of some inconsistency in the paraffin media or a result of an experimental procedure. If the paraffin media itself were inconsistent, this would be a strong reason not to use it as a synthetic soil. However, if this was the case, consistent K_p results would probably not have been achieved.

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To determine if the higher average values had any bearing on the final results for the fitted parameters and predicted frequency distribution of sorption sites, several simulations were run on the model using a fixed D_{eff} set to the maximum value obtained (7.46×10^{-9}), followed later by a simulation using the minimum D_{eff} (5.64×10^{-9}). Input files that resulted in two of the best fits for the frequency distributions (using the average $D_{eff} = 6.43 \times 10^{-9}$) were edited and run with the maximum and minimum values. Although the values for the fitted parameters changed substantially for two of the simulations done on mixed sizes, the new parameter values agreed very well with values shown to properly fit the real frequency distribution of sorption sites. Table 11 summarizes the D_{eff} values used in the simulations and the resulting fitted parameter values reported.

The starting parameter values were obtained when D_{eff} was fixed at the average described earlier. The model performed very well with this D_{eff} and seemed to converge on parameter estimates approximating reality; $\delta_{max} = 0.297$ and λ near 2. With the minimum and maximum D_{eff} values, the parameter values for experiment 3&4 are virtually unchanged and will predict very similar frequency distributions. The results for the simulation using data from experiments 4 and 6 seem to have worsened the estimates of reality. However, inspection of Figure 14 reveals that these new estimates agree with parameters shown to simulate the real distributions quite well.

Table 11: Summary of D_{eff} Values
Tested and Fitted Parameter Results

Exp	Deff	λ	δ
4&6 MIX	6.43E-09	2.855	0.287
	7.46E-09	13.384	1.104
	5.64E-09	13.299	0.954
3&4 ALL	6.43E-09	1.977	0.26
	7.46E-09	1.994	0.282
	5.64E-09	1.989	0.245

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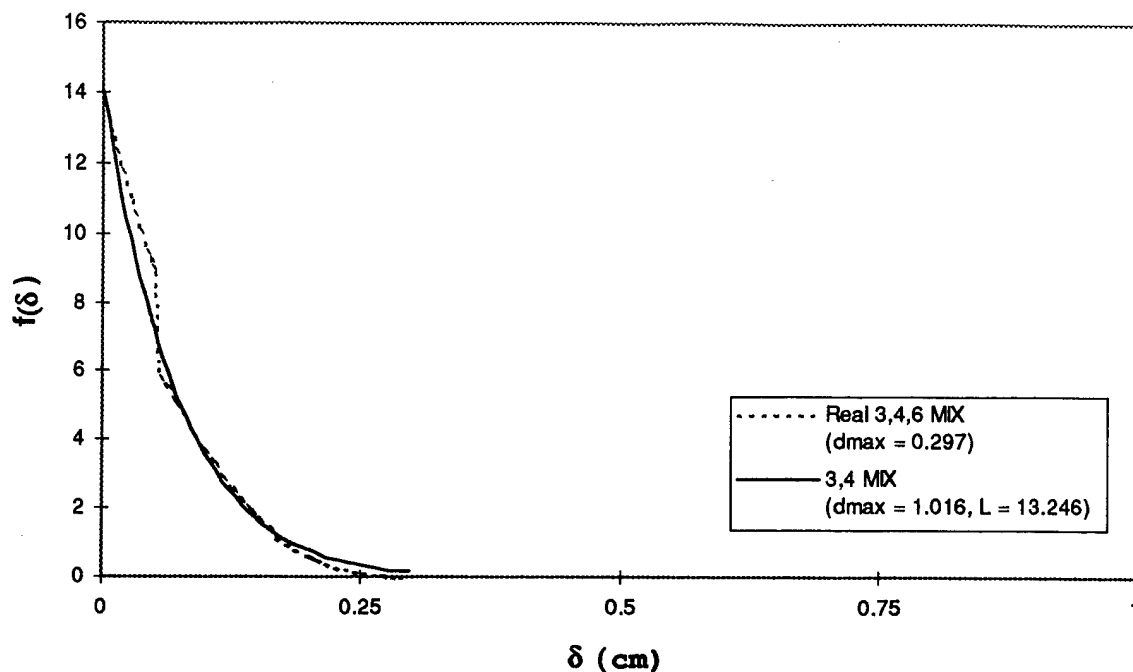
Figure 14: Frequency distribution of sorption sites using fitted δ_{max} (dmax) and λ (L)

Figure 14 shows the frequency distribution of sorption sites using parameters estimated from an input file where multi-experiment data was used (3,4 MIX). The correct fit to reality was maintained. The ability of the model to fit the correct frequency distribution with seemingly incorrect parameters is discussed further in the next section.

It may be concluded that the effect of the higher D_{eff} values for the large spheres probably has little bearing on the fits of the frequency distribution but may influence the estimates for the parameter values. Although the average was slightly higher for the large spheres, the difference is so minimal as to have almost no effect.

Particle Shape Parameters (δ_{max} and λ): Model runs were performed by either fitting for one or two parameters, and using either single or multiple experiment rate data in the input file. Model runs fitting just λ resulted in seemingly reasonable values. However, a one parameter fit is not a sufficient test for the model so two parameter fits for δ_{max} and λ were performed. With perhaps only two exceptions (experiment 3BM and

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4BM), the two parameter fits using single experiment data predicted values that did not

approximate the known parameter values. Of the two possibly reasonable model fits

both predicted the correct frequency distribution when compared graphically with reality

as in Figure 15:
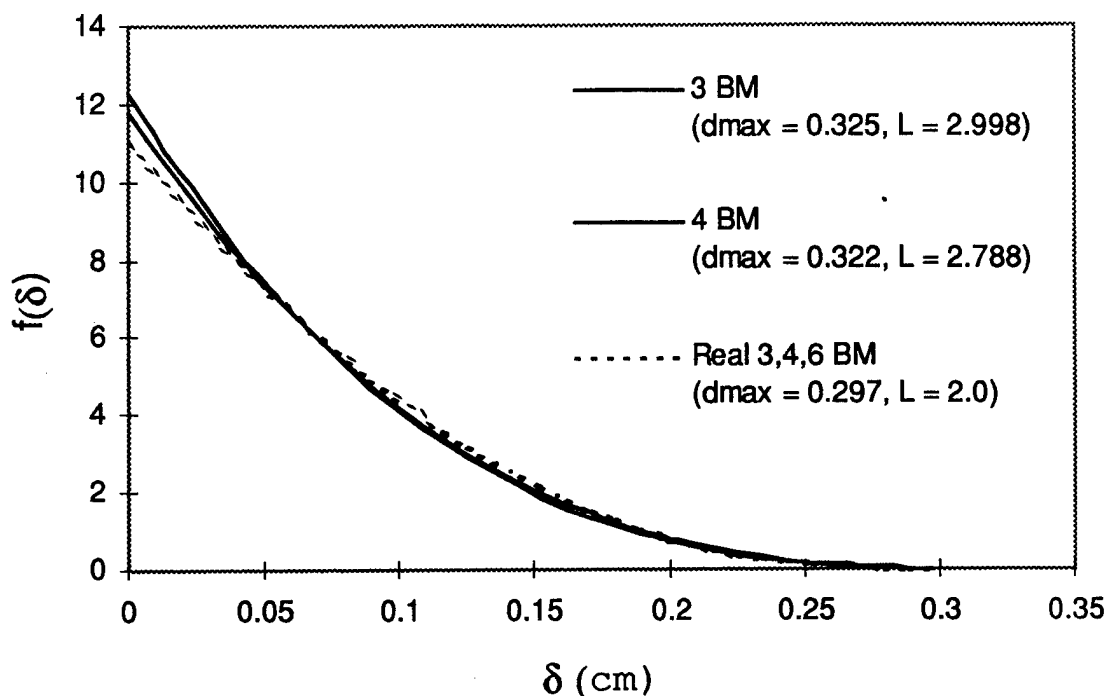
Figure 15: Frequency distribution of sorption sites: fitted and real

The remaining two parameter, single experiment fits were also plotted despite

the questionable parameter values. Several of these matched reality well while others

were inconsistent with the known frequency distributions. Next, the model behavior

was studied by simultaneously fitting data from multiple experiments of the same type.

For example, rate data from three separate aliquots all containing the same mixtures

(mass fractions) of spheres was included in one input file. Results from these

experiments also seemed to predict very odd shape parameters. The fitted δ_{max} and λ

values most often did not approximate the known estimates for either factor. However,

when these results were used to generate a frequency distribution plot, excellent fits to

the known distribution of sorption sites were obtained for all experiments. Figure 16 serves as an example of model performance in fitting the real frequency distributions of sorption sites for single and multiple data runs, and for one or two parameter fits. Only the two parameter fits using single experiment data (two-fit 1BM and two-fit 2BM) failed to predict the real sorption site distribution.

Although the model did not always fit individual parameter values approximating the real estimates, the combination of both parameters produces a distribution very like the known true sorption site distribution. This implies that multiple solutions exist for parameter values that accurately describe the real frequency distribution. In general, the model predictions of the frequency distributions when two parameter, multiple experiment data was used seems to be consistent with reality. The model appears to favor multiple experiment data when fitting the shape parameters, although no advantage was seen for using more than two sets of experimental results in one input file. The results of all model runs and graphical representations of the real and predicted frequency distributions are contained in Appendix D.
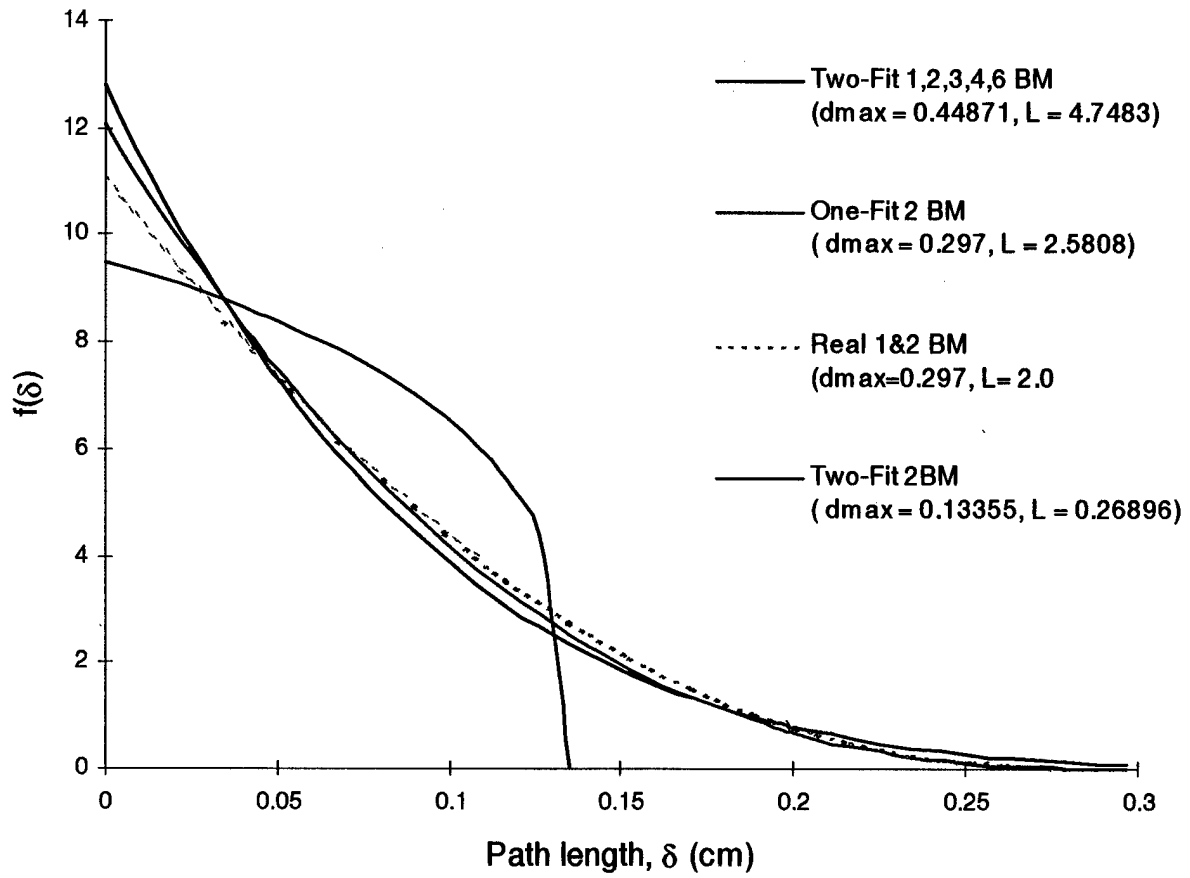
Figure 16: Experiment 1&2BM results from MSS parameter fits

IV. SUMMARY AND CONCLUSIONS

The purpose of this study was to develop a protocol for a suitable synthetic soil for use in sorption mass transfer studies leading to methods of validating sorption mass transfer models. In particular, one proposed model was the focus of this study: the Multiple Sites in Series (MSS) model developed by Heyse (1994). Synthetic soils may present a valid mechanism by which to obtain sorption rate data through batch experiments that can be used to test model response under known conditions. These known conditions include an estimate of particle shapes because the synthetic soil is manufactured to a set of specifications. If the model can predict the known conditions, this is a strong indicator that the model may be suitable for use with natural soils.

To this end, paraffin was selected as a suitable synthetic model of soil organic matter for investigating grain scale sorption mass transfer by diffusion. Preliminary batch experiments confirmed consistent chemical and physical properties of the paraffin such that the possibility of obtaining reproducible results was good. Methods were developed to shape molten paraffin to the desired spherical geometry for the batch experiments. The methods employed produced shapes of consistent sorption properties as demonstrated experimentally. Batch experiments using the synthetic media produced rate data describing the sorption of the solute into the synthetic soil.

The rate data was used for creating input files to run in the MSS model. Simulations were performed using the rate data from experiments with uniform sizes of spheres and estimated an average effective diffusion coefficient, D_{eff}. Results from this part of the study revealed the possibility of a slightly higher D_{eff} for the largest of the paraffin spheres, possibly a result of methods used in manufacturing of the spheres or in experimental design. The exact cause for the slightly higher D_{eff} could not be

resolved although the magnitude of the difference apparently did not significantly effect results in the model testing part of the research. The average D_{eff} was used in all the remaining simulations to determine if the model could predict the correct values for two parameters describing the shape of the distribution of sorption sites for the synthetic soil. If the model could predict the known distribution of sorption sites using the rate data from the experiments, this was a strong indicator for model validity.

Overall, results of model predictions were very good. The model often failed to converge on individual parameter near known or real values. However, because the model was able to converge on combinations of parameters that did approximately describe the distribution of sorption sites, the desired results were achieved. Simultaneously fitting data from multiple experiments was beneficial towards achieving parameter values that described the real distribution of sorption sites. This performance demonstrated that the model is a promising alternative to other diffusion models because it could accurately describe the diffusion domain of the sorbent. Specifically, a heterogeneous mix of sorbent geometries can be described as an average geometry, and a two parameter model for describing sorbent geometries can be predicted from rate data, although more than one experiment may be necessary. Further testing of the model is warranted under conditions using both synthetic soils or natural soils.

Future studies using synthetic soils and specifically paraffin media should attempt to isolate the cause of the variable D_{eff} values. The smallest sphere sizes achievable should be made although sphere sizes should be close in size to each other. Spheres should be pre-soaked in clean solution for several days before use in sorption studies. Mass balance must be maintained so spheres must be weighed

before and after soaking and the initial concentration in an aliquot adjusted accordingly. If dexterity limitations are not a problem, latex gloves or finger cots should be used in shaping and smoothing the spheres to rule out human skin oils as a possible diffusion limitation due to a surface film on the exterior of the sphere.

GLOSSARY

A Total mass of contaminant per unit volume of media, all phases, $M\,L^{-3}$

C_L Solution phase solute concentration, $M\,L^{-3}$

D_{eff} Effective diffusion coefficient, $L^2\,t^{-1}$

J Mass flux, Fick's Law, $M\,L^{-2}\,t^{-1}$

F Fraction of equilibrium sites

f final

i initial

j Compartment designator

K_p Equilibrium partition coefficient, $L^3\,M^{-1}$

r radius, L

S Sorbed phase solute concentration $M\,M^{-1}$

T Tortuosity factor

t time, t

V_L Volume of solution, L^3

V_R Volume of solution removed from aliquot

V_s Volume of sorbent, L^3

x distance, L

δ Diffusion path length, L

ϕ Particle porosity, $L^3\,L^{-3}$

λ Shape factor

ρ_s Dry solid density, $M\,L^{-3}$

1. HPLC Calibration

Anthracene standards used for calibration of the HPLC are noted in Table A-1.

This table is used to derive parameters describing the calibration curve and later for

determining aliquot solution concentrations based on reported HPLC peak areas.

Table A-1: HPLC Standards for Calibration Curve

Calibration Data 6/18/96	Standard Concentrations (mg/L)					
	5.11	**2.98**	**1.33**	**0.688**	**0.115**	**0.0135**
Peak	13677000	9892600	5636600	3254600	624260	84857
Area:	13658000	9876400	5642900	3287400	639070	88109
Average	13667500	9884500	5639750	3271000	631665	86483

The equation describing the calibration curve for the concentration of

anthracene in the aliquot solution is of the form:

$$C_l = 1.39 \times 10^{-7} PA + 1.71 \times 10^{-14} PA^2$$

where PA is the peak area reported by the HPLC integrator.

2. HPLC Controls:

Before running analyses on the HPLC, either standards or initial conditions were

analyzed to ensure the instrument was reporting accurate information. Concentrations

in the initial condition samples are plotted on the control charts below for experiment

1&2 (figure (A-1)), experiment 3&4 (figure (A-2)) and experiment 6 (figure (A-3)) with

the respective upper and lower 95% confidence interval demonstrating HPLC

performance. Initial condition results show consistent performance from the HPLC over

the course of the experiments. The last data point in both figure A-2 and A-3 is slightly

below the lower confidence limit. The day these samples were analyzed, a vacuum

degasser was used with the HPLC instead of purging the mobile phase with helium gas

as had been done for all previous samples. This had an unexpected effect on the results which was a slightly lower reported value for the peak area. Although the reason for this is uncertain, this result had negligible effect on the sample results.
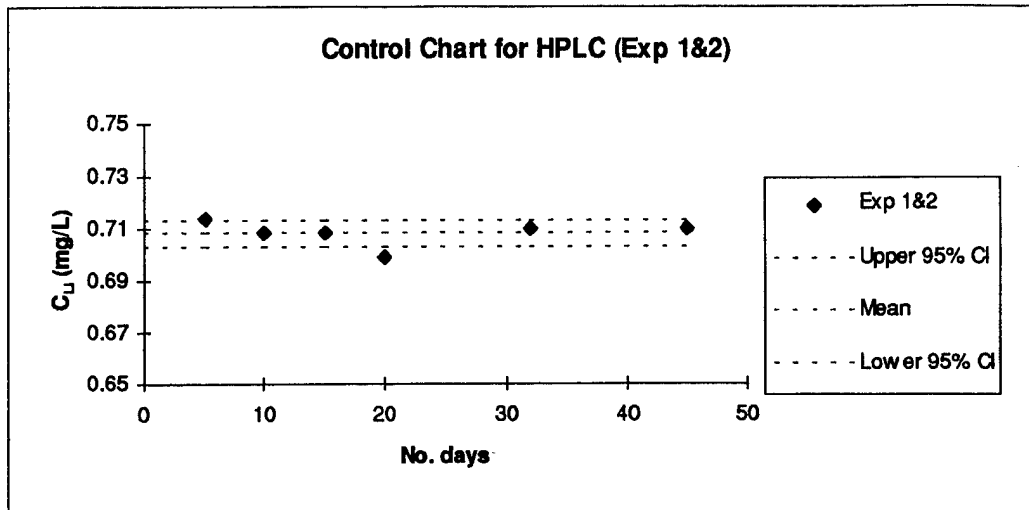
Figure A-1

Figure A-2

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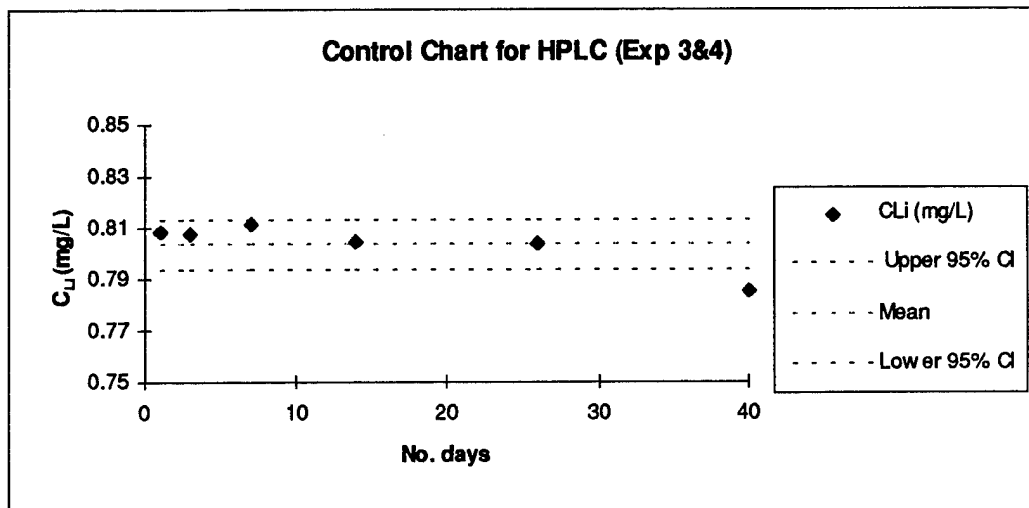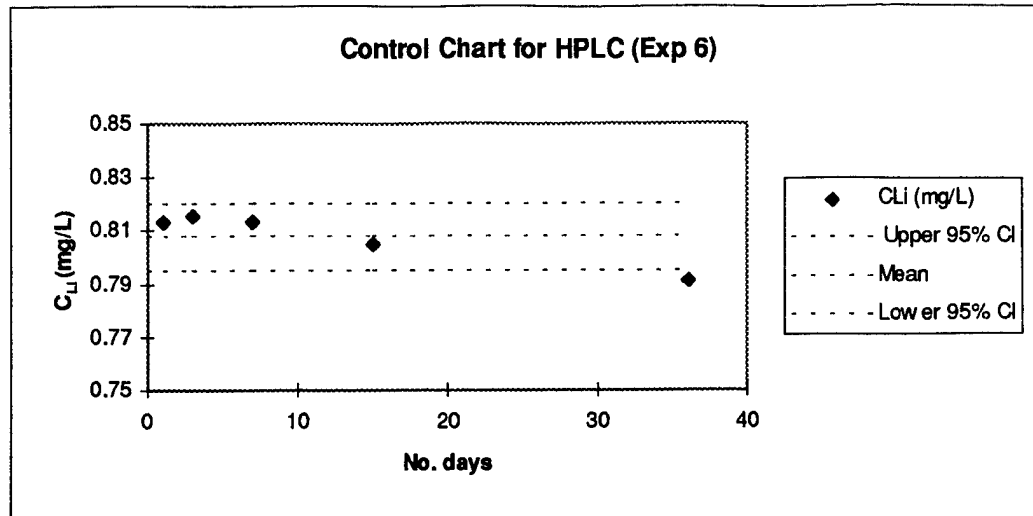
Figure A-3

3. Shredded Paraffin Aliquot Data for K_p Determination

The data in Table A-3 is for aliquots used in determination of K_p. The fraction of starting stock solution concentration is noted in aliquot name with 0,1,2, or 3 designating the heating time, "a" or "b" noting the aliquot and replicate, and "NO" indicating a blank.

Table A-3: Summary of Aliquots Prepared for Determining K_p

Aliquot	Vol Solv (m l)	Mass wax (g)	Mass solv (g)	Conc. In Solv (m g/l)	Conc. In Wax (m g/l)	S/C (m L/g)
.25 NO	4.738	0	4.3683	0.172	0.000	-
0a	4.208	0.436	3.8797	0.087	0.816	9.34
0b	4.399	0.43	4.0558	0.091	0.830	9.17
.25 NO	4.243	0	3.9124	0.174	0.000	-
1a	4.421	0.48	4.0759	0.090	0.776	8.62
1b	4.353	0.463	4.0132	0.089	0.805	9.07
2a	4.325	0.418	3.9881	0.092	0.853	9.28
2b	4.302	0.434	3.9665	0.092	0.815	8.86
3a	4.162	0.522	3.837	0.081	0.741	9.09
3b	4.154	0.586	3.8299	0.078	0.680	8.69
.5 NO	4.632	0	4.2705	0.352	0.000	-
0a	4.331	0.464	3.9931	0.174	1.657	9.50
0b	4.355	0.503	4.0153	0.170	1.571	9.22
.5 NO	4.423	0	4.0778	0.352	0.000	-
1a	4.42	0.451	4.0756	0.185	1.629	8.79
1b	4.256	0.552	3.9244	0.166	1.434	8.66
2a	4.542	0.382	4.1876	0.197	1.837	9.31
2b	4.43	0.461	4.0845	0.178	1.671	9.41
3a	4.426	0.528	4.0809	0.165	1.564	9.48
3b	4.389	0.562	4.047	0.159	1.501	9.42
.75 NO	4.666	0	4.3017	0.550	0.000	-
0a	4.111	0.639	3.7905	0.224	2.096	9.36
0b	4.155	0.49	3.831	0.256	2.489	9.72
.75 NO	3.998	0	3.6864	0.530	0.000	-
1a	4.371	0.484	4.0301	0.259	2.439	9.41
1b	4.366	0.504	4.0256	0.257	2.360	9.17
2a	4.375	0.529	4.0337	0.248	2.332	9.41
2b	4.358	0.542	4.0177	0.240	2.324	9.67
3a	4.36	0.544	4.0203	0.242	2.302	9.51
3b	4.368	0.516	4.0272	0.250	2.371	9.50
1.0 NO	4.308	0	3.9721	0.724	0.000	-
0a	4.315	0.448	3.9786	0.360	3.507	9.75
0b	4.315	0.477	3.9786	0.355	3.328	9.36
1.0 NO	3.901	0	3.5966	0.706	0.000	-
1a	4.327	0.555	3.9896	0.330	2.938	8.91
1b	4.463	0.487	4.1146	0.359	3.187	8.88
2a	4.338	0.476	3.9997	0.352	3.232	9.18
2b	4.188	0.52	3.8615	0.327	3.054	9.33
3a	4.277	0.545	3.9436	0.330	2.958	8.97
3b	4.388	0.565	4.0459	0.332	2.910	8.76

4. Sorption Isotherms for Shredded Paraffin Aliquots

Individual sorption isotherms for the aliquots prepared in determination of K_p are presented by heating time in Figures A-4 through A-7.

Sorption Isotherm for Unheated Paraffin Aliquots
Equilbrated 18 days
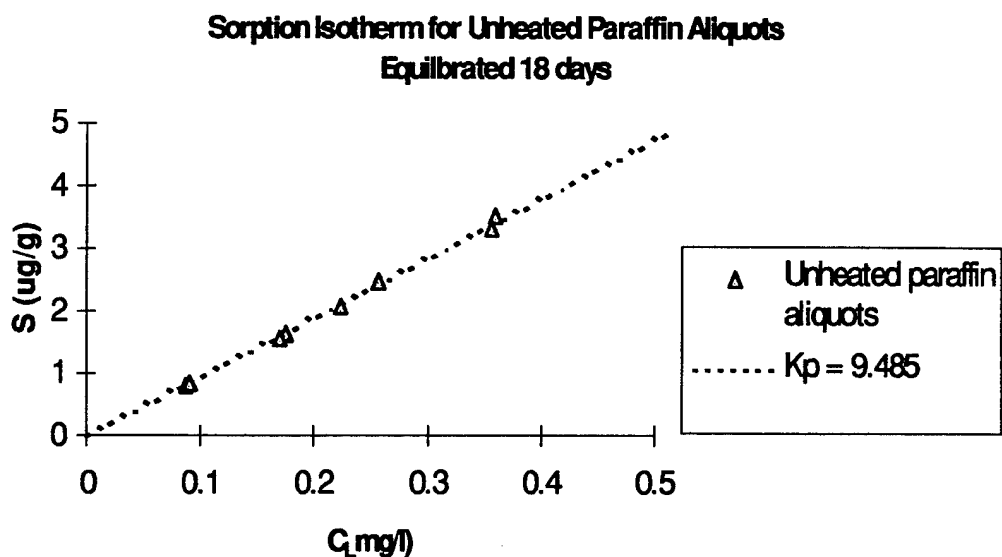
Figure A-4: Unheated paraffin sorption isotherm

Sorption Isotherm for Paraffin Heated One Hour
Equilbrated 13 days
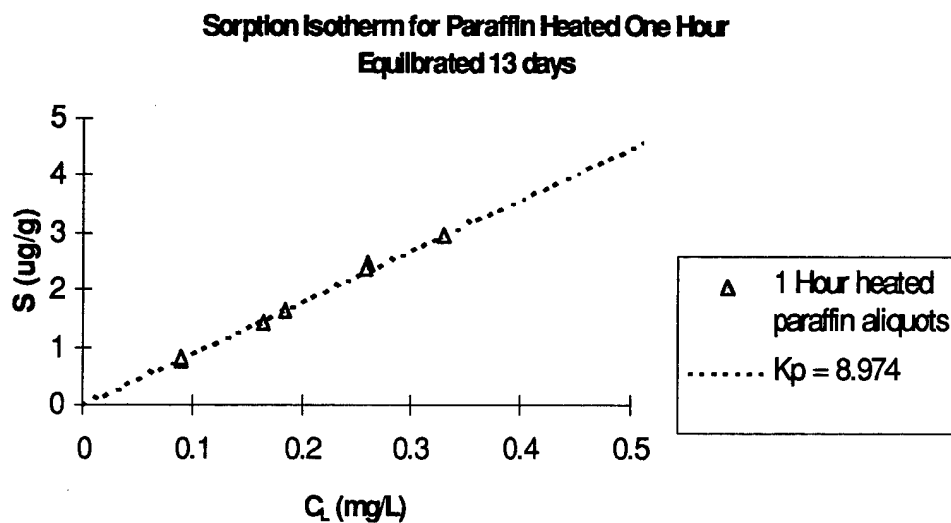
Figure A-5: One hour heat time aliquots

Sorption Isotherm for Paraffin Heated Two Hours
Euilibrated for 13 days
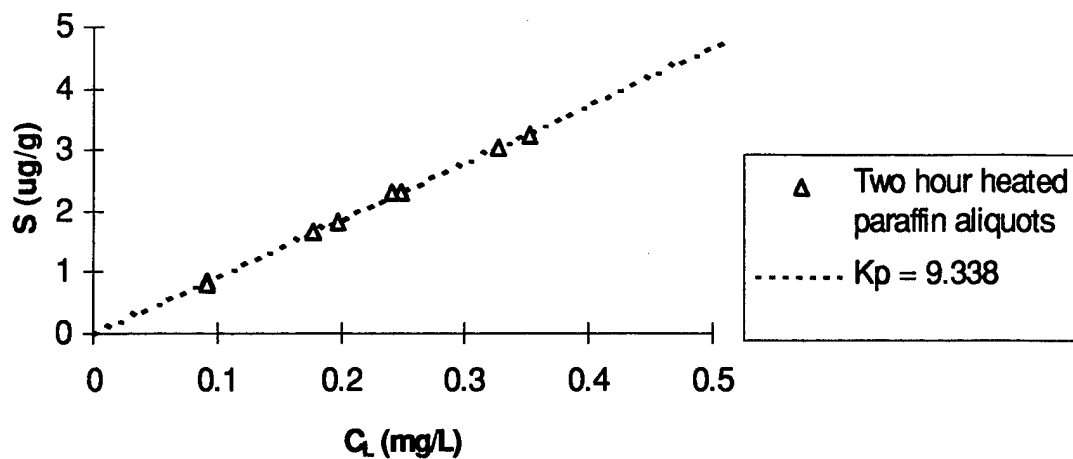
Figure A-6: Two hour heat time aliquots

Sorption Isotherm for Paraffin Heated Three Hours
Equilibrated for 13 days
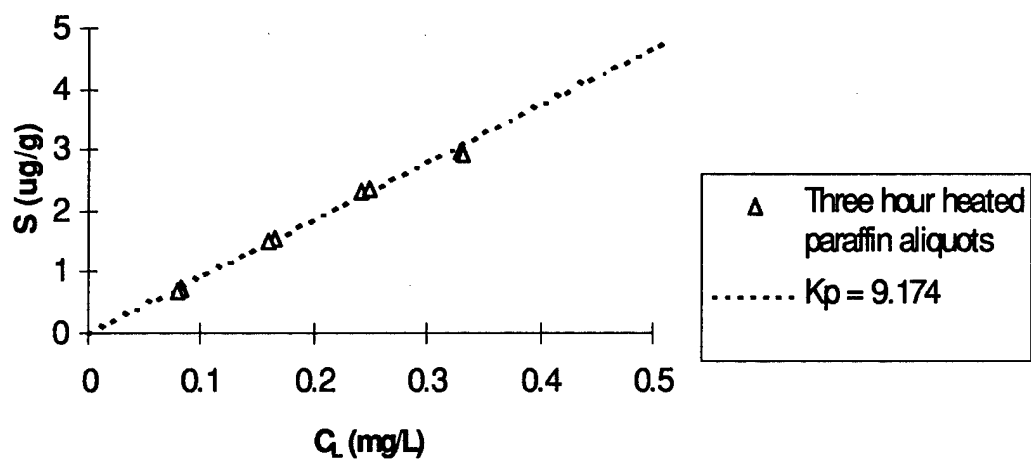
Figure A-7: Three hour heat time aliquots

5. Statistical analysis on the K_p results are presented in the following tables. $K_p{\sim}0$ through $K_p{\sim}3$ represent the heating times or treatments:

Table A-4: ANOVA for 95% Confidence Level that Mean K_p between heating times are the same

Anova: Single Factor	(Level of Significance = .05)					
SUMMARY						
Groups	Count	Sum	Average	Variance		
Kp`0	8	75.42025	9.427531	0.046211		
Kp~1	8	71.51716	8.939645	0.071325		
Kp~2	8	74.45915	9.307394	0.052172		
Kp~3	8	73.40466	9.175583	0.117748		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.048448	3	0.349483	4.863127	0.007583	2.946685
Within Groups	2.012186	28	0.071864			
Total	3.060634	31				

The magnitude of the P-value is less than the level of significance so the means for the K_p values of the four heating times are not equal at the 95% confidence level. The one hour heat time sample results are slightly lower. When the one hour results are omitted from the ANOVA, all means are the same as Table A-5 shows. A Tukey analysis of the means shows that there are two groups that are not significantly different from each other. The Tukey results are presented in Table A-6. Based on these results and the linear isotherms, the average K_p was used that included all heating times.

Table A-5: ANOVA with only 0, 2, and 3 hour heat time aliquots

Anova: Single Factor (Level of Significance = .05)						
SUMMARY						
Groups	Count	Sum	Average	Variance		
Kp`0	8	75.42025	9.427531	0.046211		
Kp~2	8	74.45915	9.307394	0.052172		
Kp~3	8	73.40466	9.175583	0.117748		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.254093	2	0.127047	1.763473	0.195905	3.466795
Within Groups	1.512913	21	0.072043			
Total	1.767006	23				

Table A-6: Tukey analysis of means using Statistix 4.1

```
STATISTIX 4.1
TUKEY (HSD) PAIRWISE COMPARISONS OF MEANS

                       HOMOGENEOUS
VARIABLE      MEAN     GROUPS
----------   ---------   -----------

Kp0          9.4275    I
Kp2          9.3074    I
Kp3          9.1756    I I
Kp1          8.9396    .. I


THERE ARE 2 GROUPS IN WHICH THE MEANS ARE
NOT SIGNIFICANTLY DIFFERENT FROM ONE ANOTHER.

CRITICAL Q VALUE   3.862   REJECTION LEVEL      0.050
CRITICAL VALUE FOR COMPARISON        0.3661
STANDARD ERROR FOR COMPARISON        0.1340
```

B. Protocol for Making Paraffin Synthetic Soil

Methods used for manufacture of the paraffin spheres used in the sorption experiments are presented here so that they may be recreated for future sorption studies. Two processes were used to shape the paraffin during these experiments, although the second method is preferred because it was less tedious. This involved use of an open ended mold into which molten paraffin was poured and cooled before shaping. The other method involved hand rolling the paraffin. Creation of a mold for shaping the paraffin into perfectly round spheres was not possible although several attempts were made to do so. This is still a possibility worth pursuing however if some of the physical and chemical characteristics of paraffin can be overcome. In particular, the amount of volume reduction upon cooling was a significant limitation of a closed mold. Working with molten paraffin is also a delicate operation to avoid burns. A description of an open ended mold follows. A similar mold, when used together with a smoothing and sizing template, gave very consistent shapes in these experiments. The template is also described here:

Mold: Use a stainless steel plate at least 25% greater in thickness than the sphere diameter desired. A plate should be small enough to handle comfortably and yield approximately ten paraffin cylinders for shaping. Several molds made during these experiments used 3X3 inch plates. The plate should be drilled through with holes of the same diameter as the spheres desired. Nine holes arrayed 3X3 were used for molds made during this experiment. Create a mold for each size of sphere if possible.

Sizing and Shaping Template: Several thin gage steel templates were made during the experiment to ensure the paraffin spheres were uniform as possible and consistent between experiments. Templates were roughly 2x2 inch and 1/16th inch thick. Three holes were drilled in templates matching the diameter of the desired spheres. The diameter should match the diameter of the holes in the molds.

The spheres were prepared as follows:

- Select a pure grade paraffin wax with at least 99% purity. Confirm purity through analytical results on shredded paraffin samples allowed to equilibrate for several days in pure methanol.

- Once purity is strongly supported, weigh out the required amount of paraffin for the number of spheres needed. Enough to fill a 50 or 100 ml beaker to the 25 ml mark with melted paraffin is a reasonable estimate.

- Place the raw paraffin material in a 50 or 100 ml glass beaker and place the beaker on a hot plate at a low temperature (70-100 °C). Monitor the melting process to ensure paraffin is not too hot or splattering of the paraffin will result.

- Place the open ended mold on top of a layer of aluminum foil on a smooth flat surface.

- Once all paraffin is melted, remove the beaker from the hot plate using heat gloves or forceps.

- Pour the molten paraffin into the holes in the top of the mold while pressing down on the mold to prevent molten paraffin from leaking out of the bottom of the mold. If the paraffin is too hot, the mold will leak at the bottom. Allow the paraffin to cool slightly and try again. Fill the holes in the mold in timely succession to avoid hardening

of the paraffin during the pouring process. Fill the holes just slightly above the rim of the mold and allow to cool to the point where paraffin is still warm and malleable.

- Extract cooled paraffin from the holes by pushing with a dowel rod of suitable diameter. The shapes at this point should resemble a cylinder of the desired diameter for the spheres to be created. Extract only about half the spheres at first and shape those to avoid hardening of some of the remaining spheres during the next phase of shaping.

- Immediately begin sizing down the paraffin cylinders by gradually turning them in the template hole corresponding to the desired sphere size. Do not force the paraffin through the hole at first as the paraffin may break apart. Once the spheres just fit through the hole and can be freely rotated in any direction, the shaping is complete.

- Segregate finished spheres by size. Place completely shaped spheres in vials designating the respective size

- Continue the process for the desired number of spheres. Keep paraffin on the hot plate while shaping the paraffin extracted from the mold. Refill the mold with molten paraffin when cooled paraffin is extracted.

- Paraffin coated glass balls were prepared by quickly dipping the selected size ball individually in molten paraffin. Small forceps were used to hold the ball during submersion. The glass balls were only dipped twice and were rounded by hand to fully distribute the paraffin on the glass surface left uncoated by the forceps. The balls were cooled between applications of the paraffin. The coated ball was then turned and smoothed in the template hole for the size desired. For these experiments, 4mm glass balls were used and then smoothed in the medium size hole (0.196 in dia.) in the template.

APPENDIX C
Summary of Aliquots And Results of Batch Experiments

1. Summary of Aliquot Analysis Results for Paraffin Spheres and Coatings:. Table C-1 is a comprehensive summary of all data obtained from analysis of the aliquots during the course of the experiments. Sample volumes removed from aliquots were recorded and used in mass balance equations to determine concentrations. Samples were always analyzed as close to a whole day fraction as possible and so only whole days are recorded. With few exceptions, all samples within the same experiment were run within two hours of each other.

Table C-1: Aliquot Data and Concentrations during Sorption Rate Experiments

Aliquot	Sample 1				Sample 2				Sample 3				Sample 4				Sample 5				Sample 6		
	ln Solvent (mg/l)	ln Paraffin (ug/g)	Volume Removed (ml)	No. Days	ln Solvent (mg/l)	ln Paraffin (ug/g)	Volume Removed (ml)	No. Days	ln Solvent (mg/l)	ln Paraffin (ug/g)	Volume Removed (ml)	No. Days	ln Solvent (mg/l)	ln Paraffin (ug/g)	Volume Removed (ml)	No. Days	ln Solvent (mg/l)	ln Paraffin (ug/g)	Volume Removed (ml)	No. Days	ln Solvent (mg/l)	ln Paraffin (ug/g)	No. Days
1B	0.4816	2.2971	1.3200	5	0.4204	2.8627	0.6621	10	0.3969	3.0717	0.7827	15	0.3820	3.1990	0.7542	20	0.3666	3.3089	1.1101	32	0.3636	3.3465	45
2B	0.4852	2.2472	1.1924	5	0.4216	2.8349	0.9124	10	0.3958	3.0610	0.8276	15	0.3760	3.2266	0.7877	20	0.3631	3.3296	1.0435	32	0.3543	3.3956	45
1M	0.4581	2.4393	1.4167	5	0.4014	2.9391	0.6910	10	0.3803	3.1180	0.8272	15	0.3728	3.1786	0.7672	20	0.3582	3.2903	1.0998	32	0.3565	3.3022	45
2M	0.4620	2.5594	1.3045	5	0.4098	3.0562	0.6827	10	0.3934	3.2068	0.7736	15	0.3909	3.2278	0.7707	20	0.3701	3.4030	1.0128	32	0.3671	3.4360	45
1S	0.4307	2.8611	0.9687	5	0.3892	3.2486	0.6946	10	0.3803	3.3310	0.7854	15	0.3916	3.2311	0.7618	20	0.3704	3.4102	1.0635	32	0.3650	3.4533	45
2S	0.4383	2.7799	0.9272	5	0.3998	3.2083	0.6779	10	0.3804	3.3322	0.8339	15	0.3797	3.3398	0.7949	20	0.3736	3.3898	1.3079	32	0.3649	3.4580	45
1BM	0.4670	2.4416	0.9017	5	0.4143	2.9387	0.7099	10	0.3895	3.1728	0.8028	15	0.3779	3.2648	0.7430	20	0.3654	3.3692	1.0554	32	0.3660	3.4427	45
2BM	0.4656	2.4382	1.2378	5	0.4082	2.9668	0.6693	10	0.3826	3.1936	0.5964	15	0.3773	3.2396	0.7638	20	0.3635	3.3525	1.0659	32	0.3565	3.4064	45
1-ALL	0.4559	2.5786	1.0044	5	0.4060	3.0518	0.6806	10	0.3844	3.2493	0.7784	15	0.3795	3.2923	0.7638	20	0.3690	3.3800	1.0318	32	0.3643	3.4172	45
2-ALL	0.4987	2.7870	1.1597	5	0.4502	3.3861	0.6602	10	0.4301	3.6276	0.7964	15	0.4254	3.6823	0.8069	20	0.4158	3.7901	1.0211	32	0.4063	3.8915	45
1GB	0.5639	2.8322	0.7744	1	0.5096	3.8075	0.7071	2	0.4876	4.1547	0.7800	2	0.4791	4.2842	0.7776	4	0.4699	4.4128	0.7283	5	0.4595	4.5478	15
2GB	0.5603	2.8663	0.7126	1	0.5047	3.8310	0.6824	2	0.4899	4.0736	0.5883	2	0.4784	4.2506	0.7652	4	0.4668	4.4160	0.7111	5	0.4585	4.5254	15
1MIXB	0.5104	1.5826	0.7619	1	0.4230	2.2235	0.6802	2	0.3752	2.5547	0.8141	2	0.3544	2.6690	0.6804	4	0.3372	2.7937	0.7304	5	0.2923	3.0469	15
2MIXB	0.5167	1.6208	0.6798	1	0.4292	2.3047	0.7131	2	0.3893	2.5999	0.7611	2	0.3667	2.7754	0.7557	4	0.3492	2.8698	0.7481	5	0.3048	3.1364	15
3B	0.6150	1.4831	0.5324	1	0.4991	2.2493	0.5446	3	0.4280	2.6628	0.8129	3	0.3663	2.9146	0.5831	14	0.3424	2.9907	0.8665	26	0.3252	3.0196	40
4B	0.6213	1.4009	0.5387	1	0.5107	2.1096	0.5398	3	0.4290	2.5613	0.6675	3	0.3654	2.8283	0.5908	14	0.3356	2.9245	0.8535	26	0.3248	2.9429	40
3M	0.6115	1.6962	0.5321	1	0.5142	2.4192	0.5677	3	0.4420	2.8753	0.7563	3	0.3880	3.1353	0.5944	14	0.3658	3.2160	0.8588	26	0.3474	3.2516	40
4M	0.6114	1.6645	0.5168	1	0.5079	2.4202	0.5144	3	0.4373	2.8640	0.7767	3	0.3829	3.1228	0.6014	14	0.3588	3.2098	0.8677	26	0.3523	3.2207	40
3S	0.5968	1.9663	0.5487	1	0.4891	2.8342	0.5301	3	0.4305	3.2403	0.7772	3	0.3968	3.4202	0.5841	14	0.3865	3.4623	0.8572	26	0.3825	3.4719	40
4S	0.5878	1.9318	0.5329	1	0.4849	2.7111	0.5261	3	0.4221	3.1213	0.7992	3	0.3857	3.3309	0.5764	14	0.3736	3.3465	0.8650	26	0.3673	3.3597	40
3ALL	0.6065	1.6824	0.5500	1	0.5000	2.4448	0.5272	3	0.4527	2.7351	0.7707	3	0.3794	3.0765	0.5969	14	0.3602	3.1441	0.8381	26	0.3520	3.1595	40
4ALL	0.6174	1.5819	0.5497	1	0.5022	2.4007	0.4670	3	0.4312	2.8421	0.8313	3	0.3747	3.1031	0.6012	14	0.3660	3.1682	0.8444	26	0.3466	3.1857	40
3MIX	0.6074	2.0232	0.5354	1	0.5326	2.6731	0.5603	3	0.4765	3.0970	0.7823	3	0.4247	3.3736	1.1846	14	0.3982	3.4476	0.5886	26	0.3826	3.4696	40
4MIX	0.6185	1.9105	0.5371	1	0.5325	2.6534	0.6767	3	0.4675	3.1117	0.7489	3	0.4162	3.3828	0.5946	14	0.3959	3.4617	0.8325	26	0.3872	3.4782	40
3BM	0.6058	1.677	0.5628	1	0.4975	2.4304	0.5320	3	0.4271	2.8544	0.7715	3	0.3768	3.0831	0.5740	14	0.3546	3.1595	0.8721	26	0.3486	3.1702	40
4BM	0.6145	1.6205	0.5135	1	0.5081	2.3912	0.5348	3	0.4362	2.8378	0.7835	3	0.3822	3.0917	0.5906	14	0.3633	3.1593	0.8786	26	0.3556	3.1737	40
6B	0.6341	1.3115	0.5621	1	0.5028	2.1560	0.7937	3	0.4084	2.6334	0.8332	3	0.3469	2.8699	0.5993	15	0.3181	2.9317	-	36	-	-	-
6M	0.6209	1.6177	0.5416	1	0.5014	2.5067	0.7709	3	0.4225	2.9747	0.8156	3	0.3725	3.1916	0.5876	15	0.3699	3.2348	-	36	-	-	-
6S	0.5941	1.8239	0.5623	1	0.4755	2.6888	0.7652	3	0.4052	3.0957	0.8312	3	0.3731	3.2291	0.5971	15	0.3542	3.2654	-	36	-	-	-
6BM	0.6287	1.5695	0.5760	1	0.5132	2.4166	0.7641	3	0.4294	2.9133	0.8460	3	0.3720	3.1597	0.5897	15	0.3489	3.2288	-	36	-	-	-
6ALL	0.6224	1.5317	0.5683	1	0.5028	2.3730	0.7834	3	0.4189	2.8375	0.8231	3	0.3671	3.0432	0.5679	15	0.3414	3.1165	-	36	-	-	-
6MIX	0.6175	1.9055	0.5580	1	0.5152	2.7794	0.7834	3	0.4448	3.2540	0.8441	3	0.3995	3.4754	0.5973	15	0.3697	3.5737	-	36	-	-	-
7G	0.6541	3.3734	0.9256	1	0.5868	4.5320	0.8509	3	0.5533	4.9480	0.5860	3	0.5485	4.9667	-	14	-	-	-	-	-	-	-
8G	0.6399	3.3933	0.8128	1	0.5736	4.4621	0.8338	3	0.5422	4.8471	0.5815	3	0.5364	4.9027	-	14	-	-	-	-	-	-	-

Table C-2: Estimates of Sorbed to Solution Phase Concentrations (S/C$_L$) During Experiments

days	1B	2B	1M	2M	1S	2S	1ALL	2ALL	1BM	2BM
0	0	0	0	0	0	0	0	0	0	0
5	4.769629	4.631724	5.3325039	5.539603	6.620199	6.342524	5.656667	5.588901	5.228543	5.236877
10	6.809663	6.724894	7.321432	7.458276	8.347389	8.14763	7.516801	7.521426	7.093257	7.268677
15	7.738332	7.733643	8.198717	8.14803	8.759704	8.759478	8.452484	8.434312	8.166048	8.346428
20	8.373639	8.580419	8.526801	8.25666	8.251972	8.794011	8.675508	8.656334	8.638245	8.586833
32	8.977835	9.169081	9.185293	9.195752	9.206918	9.072166	9.158635	9.115646	9.220427	9.222539
45	9.203338	9.583437	9.261676	9.331973	9.461958	9.476035	9.37984	9.577929	9.670875	9.555105

days	3B	4B	3M	4M	3S	4S	3ALL	4ALL	3BM	4BM	3MIX	4MIX
0	0	0	0	0	0	0	0	0	0	0	0	0
1	2.411773	2.254872	2.773944	2.722467	3.298138	3.286623	2.773946	2.562224	2.75273	2.637258	3.330821	3.089079
3	4.506417	4.130449	4.704615	4.765204	5.795091	5.590574	4.889997	4.780067	4.885365	4.706582	5.019403	4.982874
7	6.251286	5.984813	6.505782	6.548814	7.52608	7.394789	6.041755	6.591492	6.683476	6.505686	6.47911	6.656472
14	7.957574	7.739833	8.080942	8.155955	8.619884	8.558413	8.108587	8.280512	8.182126	8.088789	7.943295	8.128316
26	8.734852	8.71534	8.792163	8.944005	8.95753	8.956299	8.729113	8.898792	8.734852	8.734852	8.658946	8.744881
40	9.286609	9.061418	9.358873	9.141457	9.077828	9.147977	8.974825	9.190428	9.093088	8.924092	9.067926	8.982217

days	6B	6M	6S	6ALL	6BM	6MIX	days	7G	8G
0	0	0	0	0	0	0	1	5.156871	5.302535
1	2.06837	2.605334	3.069857	2.460734	2.480474	3.085839	3	7.736312	7.780226
3	4.288407	4.999428	5.654316	4.71994	4.70939	5.394547	6	8.941952	8.94046
7	6.448148	7.040723	7.639746	6.773884	6.783951	7.316186	14	9.075643	9.140359
15	8.26836	8.567771	8.654252	8.290065	8.494835	8.720649			
36	9.215343	9.011942	9.274643	9.129236	9.226642	9.667569			

days	1GB	2GB	1MIXB	2MIXB
1	5.022628	5.101066	3.100736	3.13691
2	7.486331	7.591063	5.256167	5.370259
3	8.521097	8.315562	6.808281	6.675719
4	8.942266	8.884635	7.586715	7.513313
5	9.39011	9.460193	8.285445	8.214783

2. Rate Data Plots for Paraffin Spheres and Coatings:

Legend keys do not indicate the order of the plotted points on each other. These plots show qualitatively the reproducibility achieved between experiments.
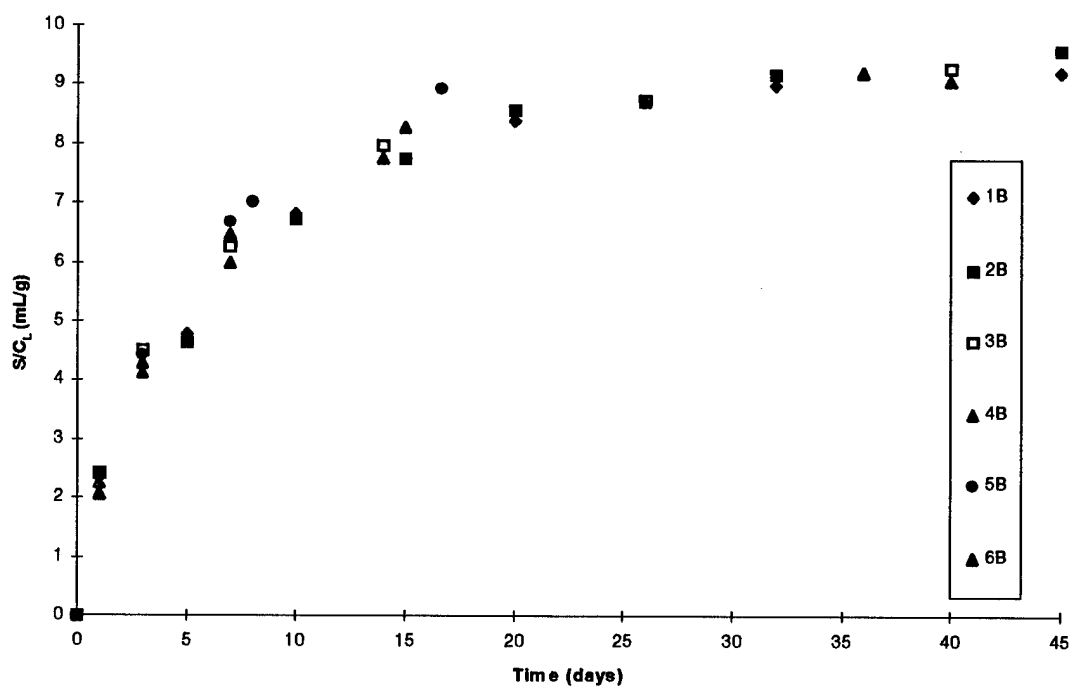
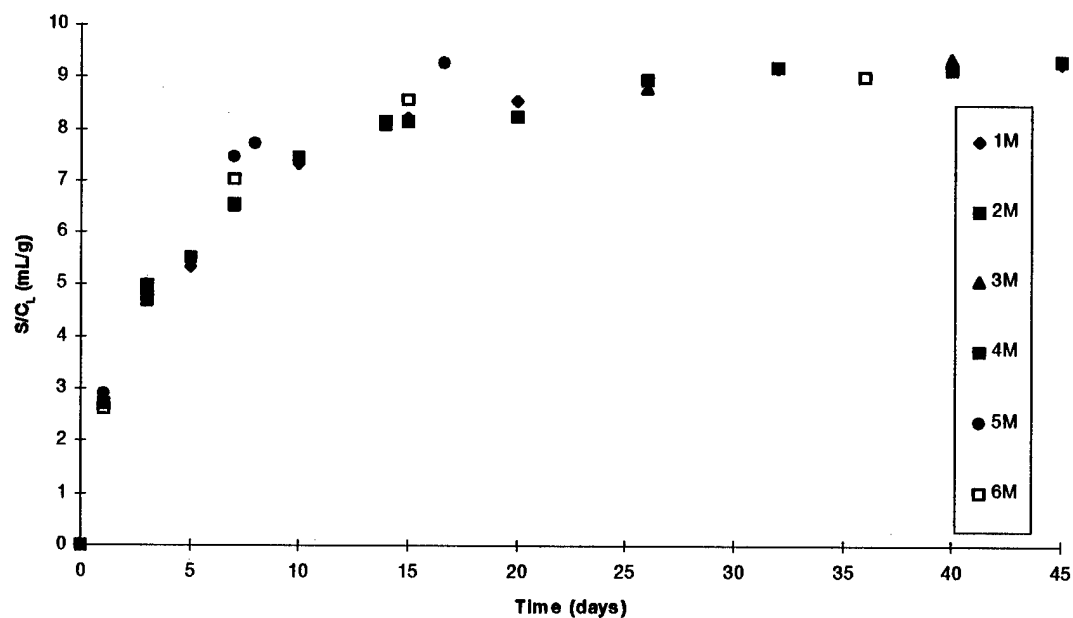

Figure C-1: Large paraffin spheres sorption rate

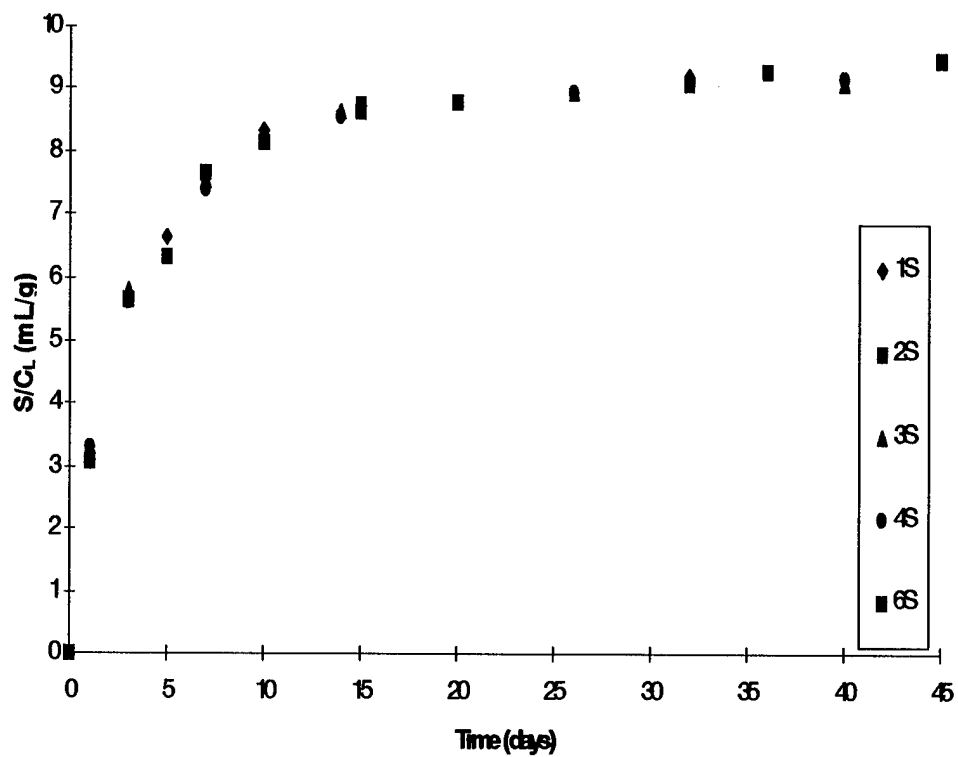Figure C-2: Medium paraffin spheres sorption rate-

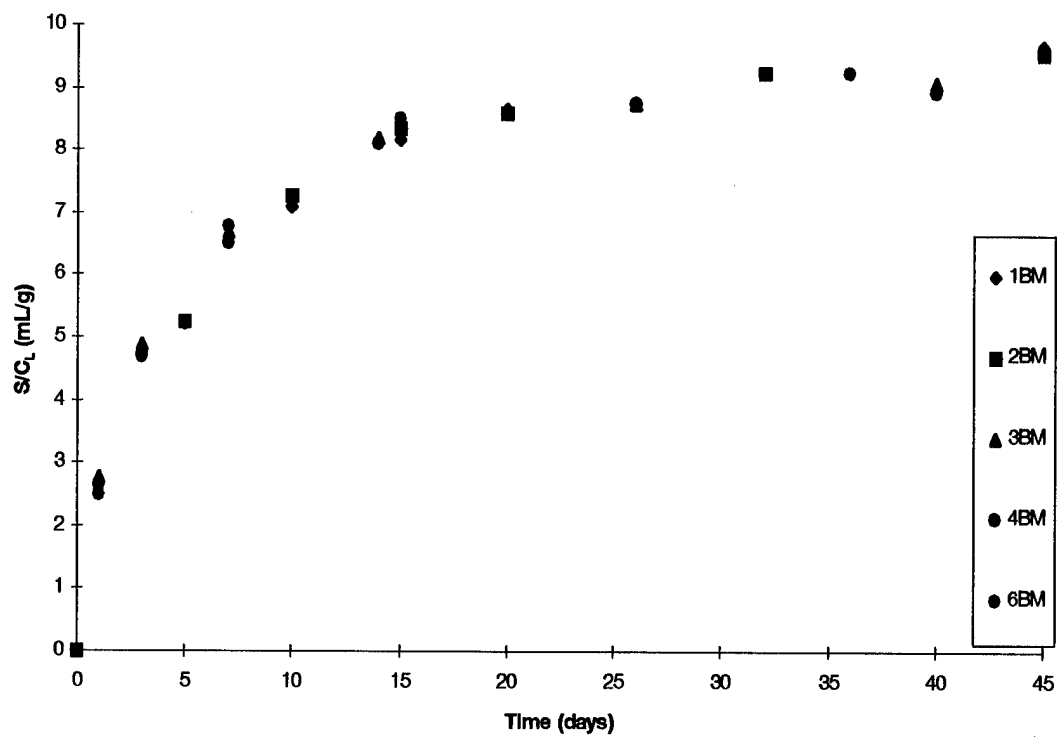Figure C-3: Small paraffin spheres sorption rate

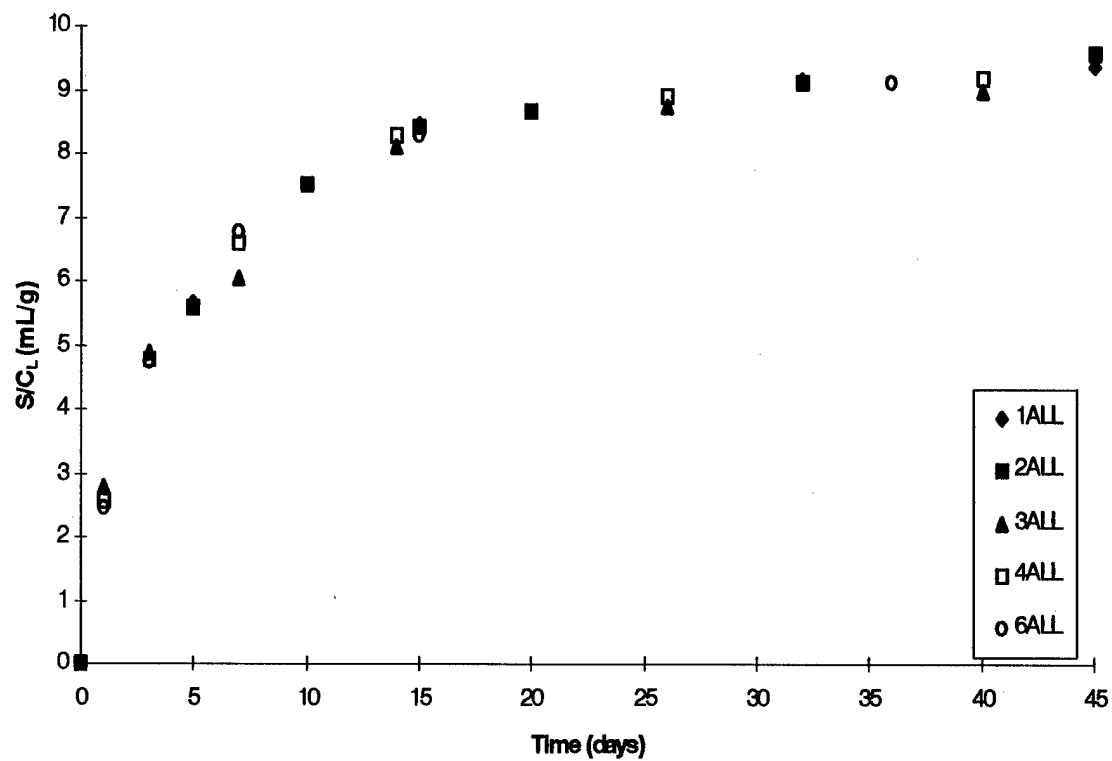Figure C-4: Large and Medium Spheres sorption rate
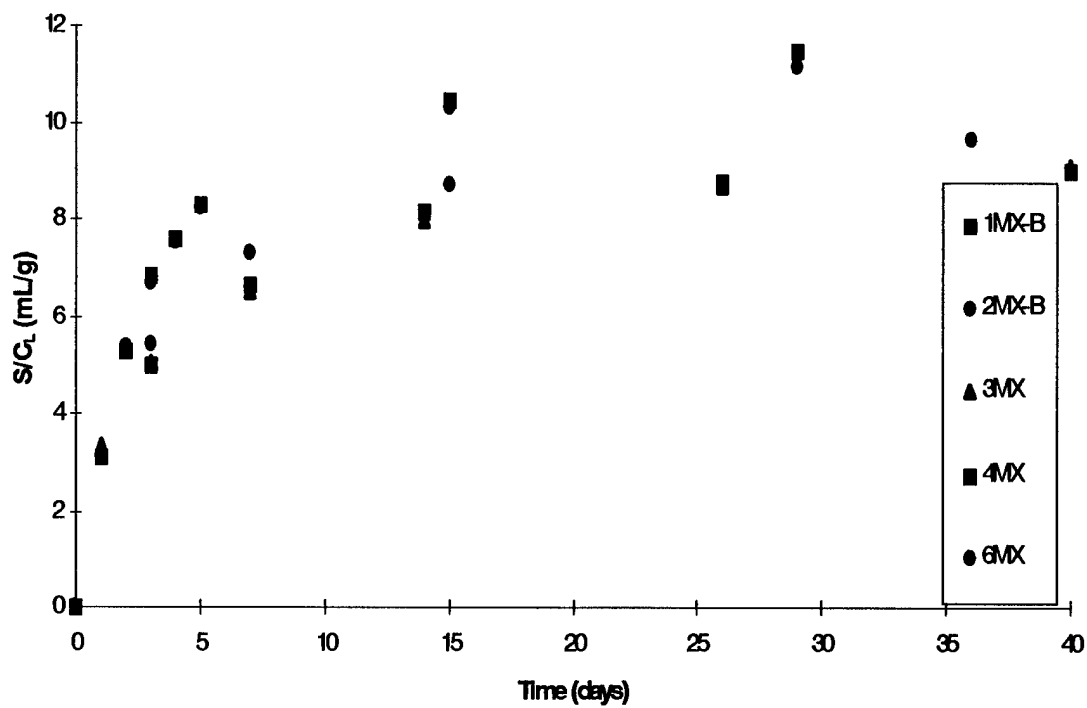
Figure C-5: ALL paraffin spheres sorption rate

Figure C-6: Mixed paraffin spheres and coatings sorption rate
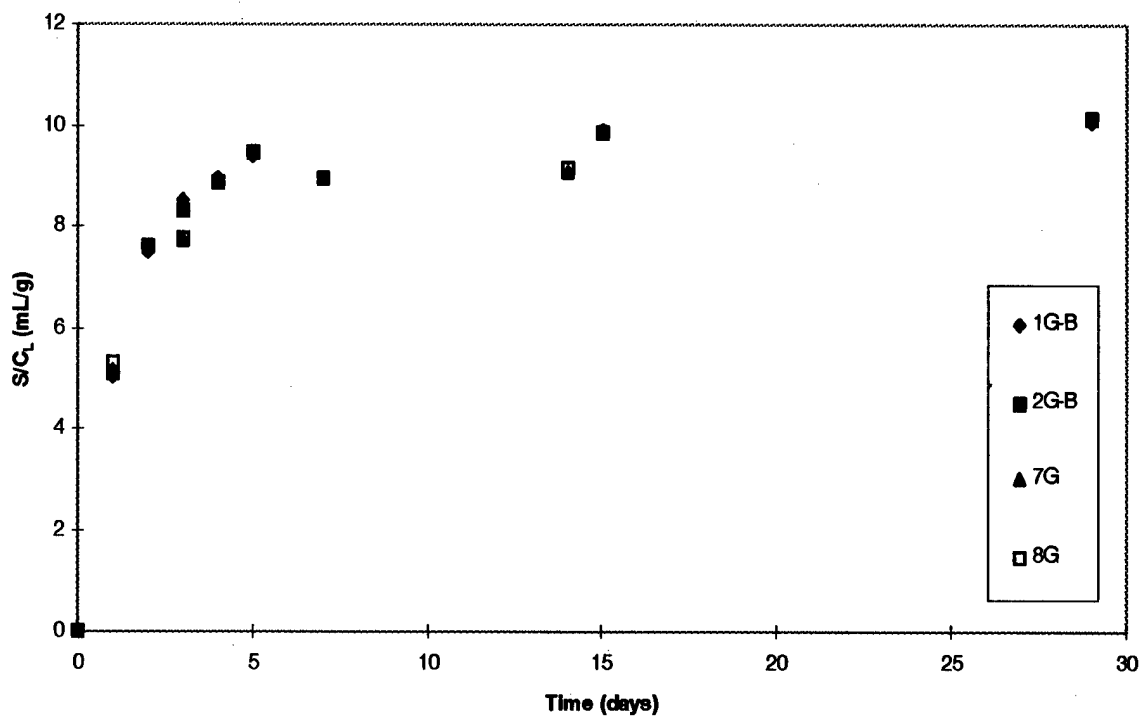
Figure C-7: Coated glass balls sorption rate

3. Blanks and Initial Condition Replicates:

Paraffin spheres made for sorption experiments were sacrificed, crushed and placed in stock solution for the duration of the experiments. These aliquots are labeled "crushed" in table C-1 below. The "control" aliquot contains uncoated glass balls. Blanks 1 and 2 contain large paraffin spheres in pure 1:1 MEOH-H2O solution. Blank 3 contains paraffin coated glass balls in 1:1 MEOH-H2O. IC~2 was not opened until the last sampling day and is the replicate for the initial condition that was used to monitor HPLC performance during the duration of the experiments. The purpose of IC~2 was to determine if degradation of the anthracene in the solution was occurring. Aliquots in Table C-3 were analyzed concurrently with the last sampling round for experiment one and two.

Table C-3: Analysis Results for Blanks, and Initial Condition Replicate

	Mass (g)				Final Conc.			
Aliquot	Paraffin	Solvent (initial)	Initial Vol Solv. (ml)	Initial Solv.Conc (mg/l)	In Solvent (mg/l)	In Paraffin (ug/g)	No. Days	Kp
1~CRUSHED	1.9612	19.6587	21.3218	0.7139	0.3751	3.59833	46	9.592
2~CRUSHED	0.5529	3.7854	4.1057	0.7139	0.3043	2.98346	46	9.804
3~CRUSHED	0.5096	3.9016	4.2316	0.7139	0.3259	3.15766	46	9.689
1~CONTROL	0.0000	17.9927	19.5149	0.7139	0.7027	0.00748	46	0.011
1~BLANK	2.0260	16.3972	17.7844	0.7139	0	0	46	-
2~BLANK	2.0455	19.9023	21.5861	0.7139	0	0	46	-
3~BLANK	2.0077	20.3071	22.0250	0.7139	0	0	46	-
IC~2	-	-	-	0.7139	0.7061	-	46	-

The estimated K_p values for the "crushed" aliquots are slightly higher than the average K_p from the shredded paraffin experiments and the average K_p from the batch studies with the paraffin spheres. This may be the result of instrument drift on the analysis day, a slight amount of anthracene degradation, or perhaps a longer equilibration time, resulting in a lower peak area reported and therefore solution

concentration. IC~2 results agreed very well with the initial condition ran the previous day but drifted slightly lower from the initial concentration ran the first sample day. Again, this may be attributed to a drift in the instrument or perhaps anthracene degradation. The results of a slight drift are magnified through the calculations resulting in a seemingly different value of K_p when in reality the results are very consistent. For comparison, a shredded paraffin aliquot which had been prepared for the rate data experiment, but never used, was sacrificed on the day of the last sample round for experiment 1 & 2. The K_p results for the 78 day equilibration time were 9.496 ml/g. This value is consistent with those found for both the shredded paraffin experiments and the paraffin sphere experiments.

Unfortunately, shortly after completion of the last sampling day of experiment 3&4, the HPLC suffered a mechanical failure rendering it unusable as of this date and so no results on blanks prepared for these experiments can be reported. However, based on the observations of the rate data and results of analyses on initial conditions, the experiment appears to be consistent with experiment 1&2.

APPENDIX D
Model Parameter Estimates and Distribution Fit Results

1. Real and Predicted Frequency Distributions:

The plots below show the performance of the MSS model in predicting shape

factors that accurately describe the real distribution of sorption sites in the aliquots.

The legend identifies the plots in the order that they appear on the vertical axis, from

top to bottom. These results are for the simulations using data from aliquots containing

mixtures of sizes and shapes of paraffin spheres and coatings.

Frequency Distribution of Sorption Sites
from One Parameter Fit - Single Experiment

One-Fit 1BM
(dmax = 0.297, L = 2.5044)

One-Fit 2 BM
(dmax = 0.297, L = 2.5808)

Real 1&2 BM
(dmax = 0.297)
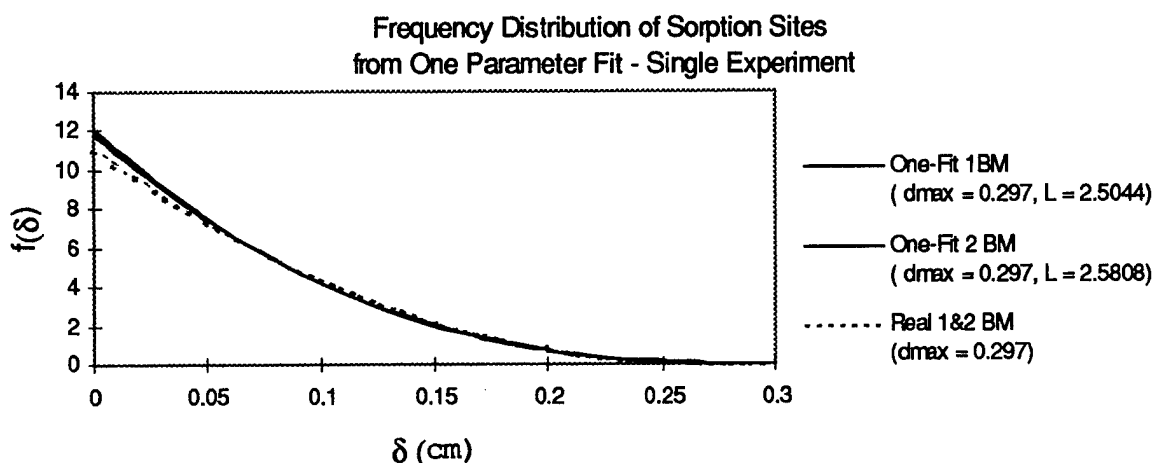
Figure D-1: One parameter fit results for MSS, 1BM and 2 BM versus real distribution

Frequency Distribution of Sorption Sites
from Two Parameter Fit - Single and Multiple Experiments

Two-Fit 1&2 BM
(dmax=0.49359, L = 5.4829)

Real 1&2 BM

Two-Fit 1BM
(dmax= 0.14425, L= 0.36788)

Two-Fit 2BM
(dmax = 0.13355, L = 0.26896)
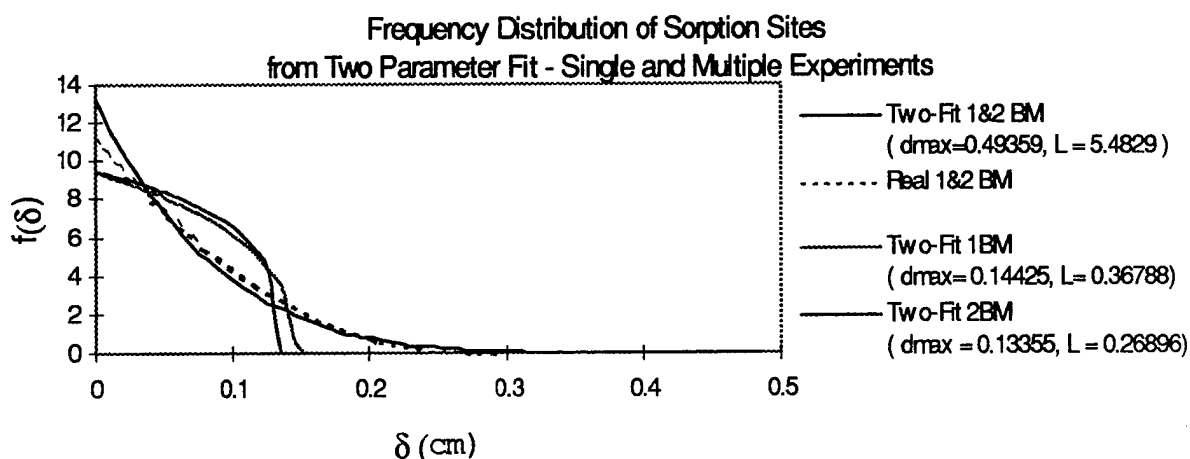
Figure D-2: Two parameter fit results for MSS, 1 and 2 BM as single or multi-experimental input

Frequency Distribution of Sorption Sites
from Two Parameter Fit - Single Experiments

3 BM
(dmax = 0.325, L = 2.998)

4 BM
(dmax = 0.322, L = 2.788)

- - - - - Real 3,4,6 BM

6 BM
(dmax =0.140, L = 0.458)
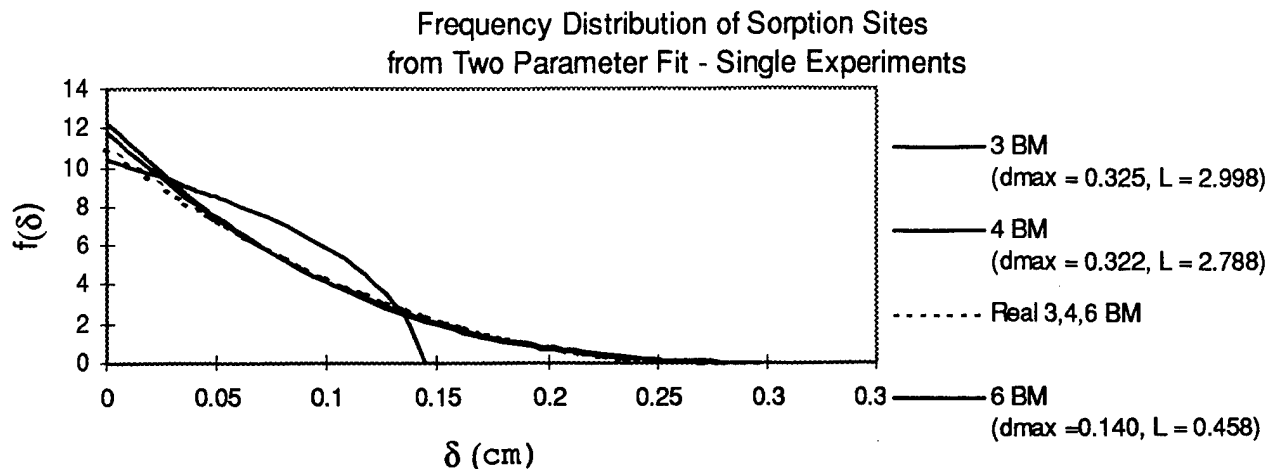
Figure D-3: Two parameter fit results for 3 and 4 BM, as single experiment

Frequency Distribution of Sorption Sites
from Two Parameter Fit - Multiple Experiments

3,4,6 BM
(dmax = 0.241, L = 1.792)

3,4 BM
(dmax = 0.315, L = 2.770)

4,6 BM
(dmax = 0.2068, L = 1.3133)

- - - - - Real 3,4,6 BM
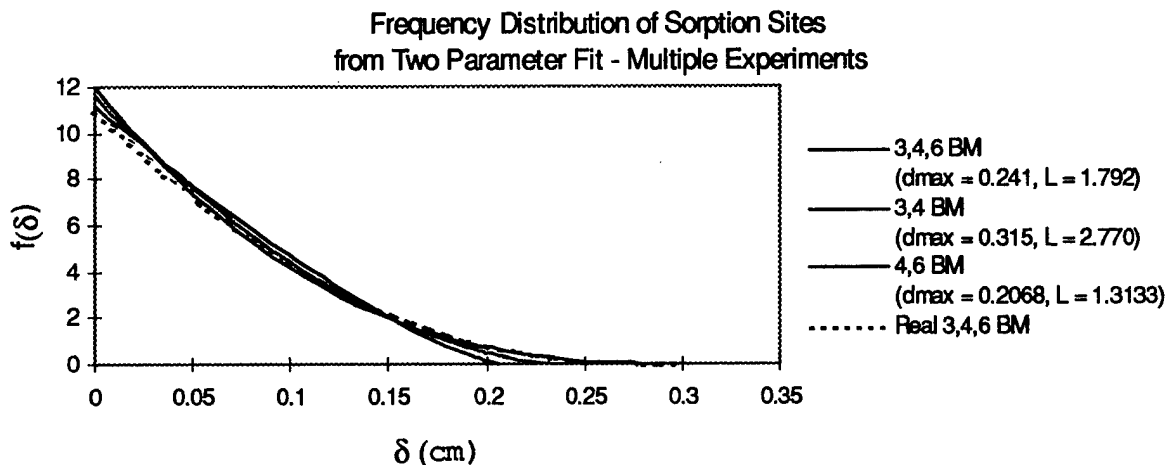
Figure D-4: Two parameter fit results for MSS using multiexperiment data, 3-6BM

Frequency Distribution of Sorption Sites
from Two Parameter Fit - Single Experiments

- - - - - Real 1&2 ALL

1 ALL (dmax = 0.158, L = 0.714

2 ALL (dmax = 0.147, L = 0.593)
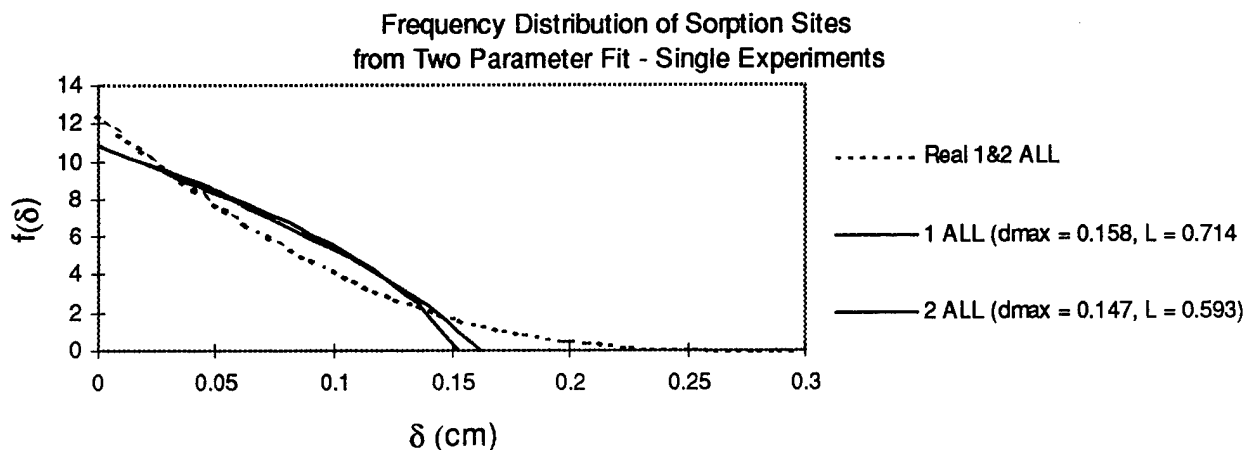
Figure D-5: Two parameter fit results for MSS using single experiment data, 1-2 ALL
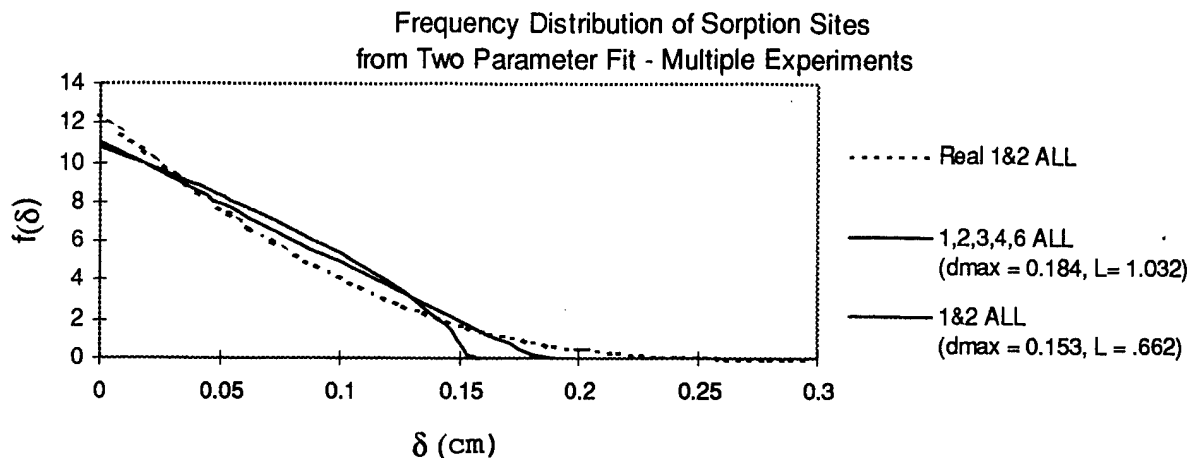
Figure D-6: Two parameter fit results for MSS using multiexperiment data
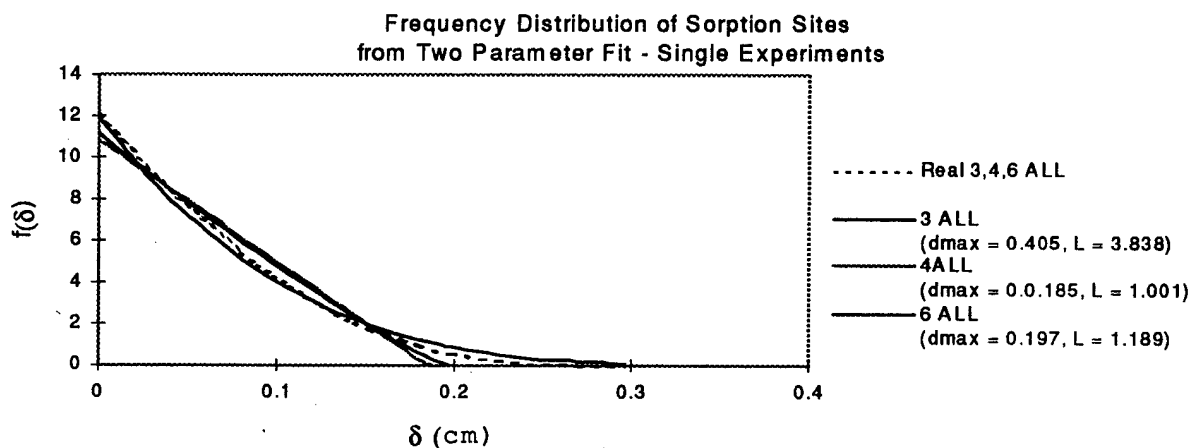
Figure D-7: Two parameter, single experiment results for experiments 3,4 6 ALL
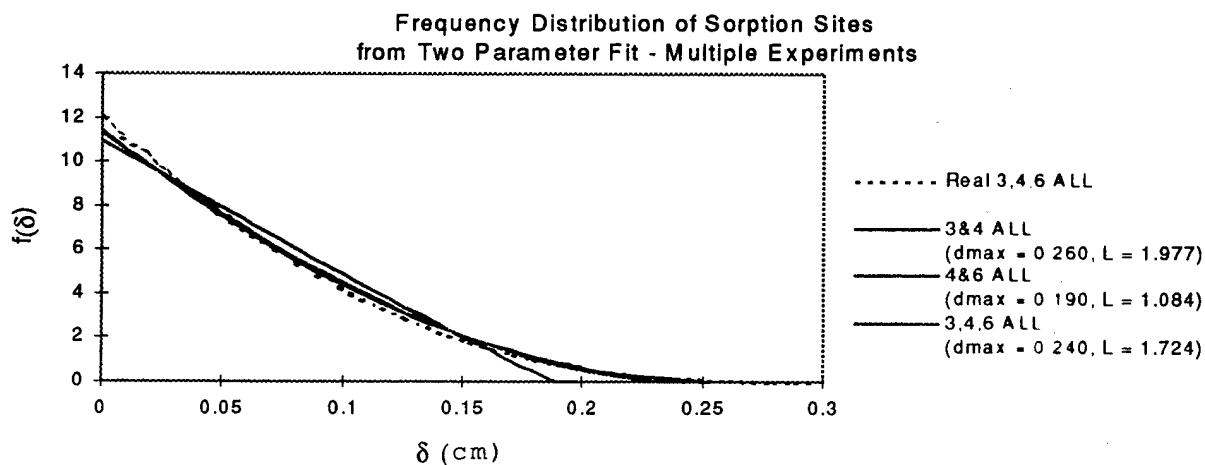
Figure D-8: Two parameter , multiexperiment data results for MSS, 3-6 ALL

Frequency Distribution of Sorption Sites from Two Parameter Fit - Single Experiments

1MXB (dmax = 0.072, L = 0.010)
2MXB (dmax = 0.072, L = 0.004)
Real 1MXB
Real 2MXB
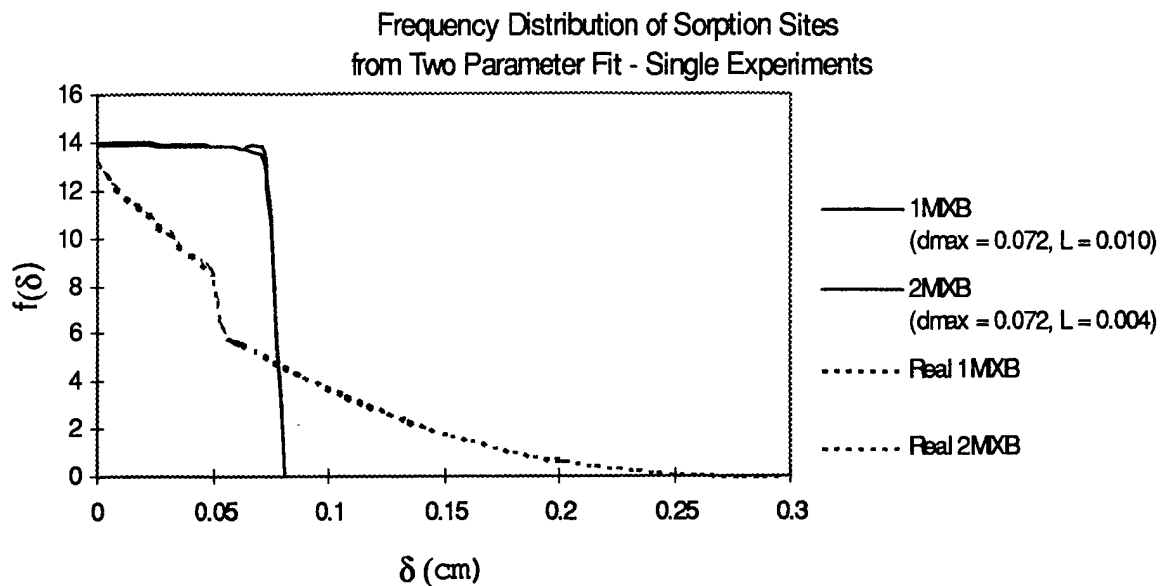
Figure D-9: Two parameter, single experiment results for 1-2 MIX

Frequency Distribution of Sorption Sites from Two Parameter Fit - Multiple Experiments

1,2,3,4,6 MX (dmax = 0.180, L = 1.763)
1,2 MXB (dmax = 0.072, L = 0.0006)
Real 1MIXB (dmax = 0.297)
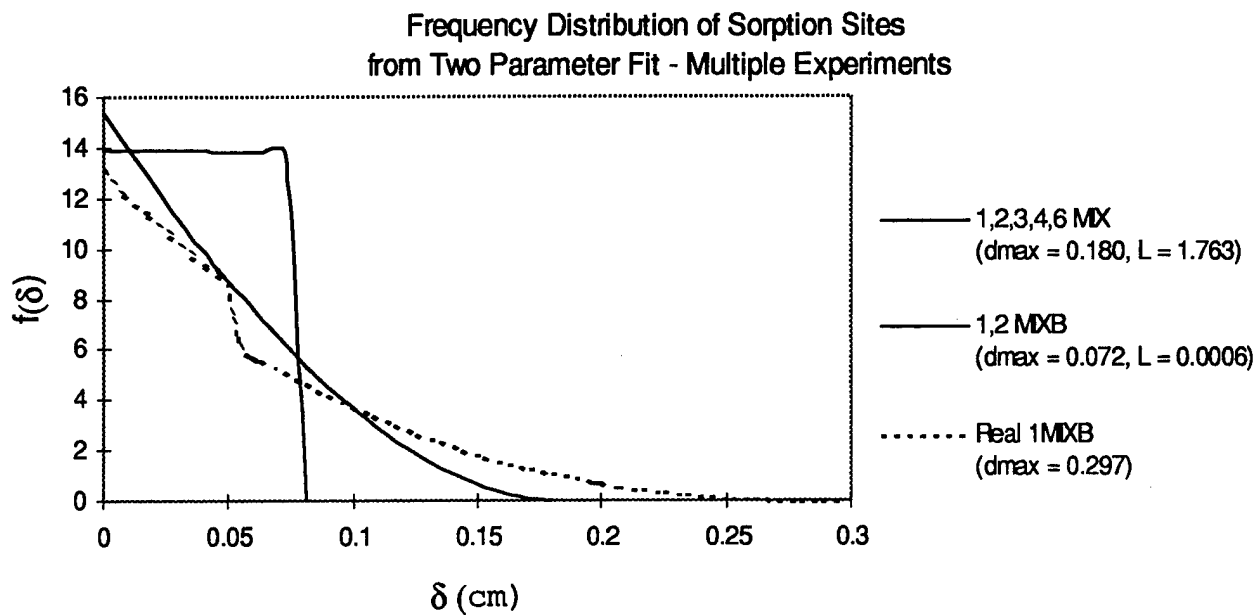
Figure D-10: Two parameter, multiexperiment results for MIX sizes

Frequency Distribution of Sorption Sites
from Two Parameter Fit - Single Experiments

3 MIX
(dmax = 1.507, L = 20.7)

Real 3,4,6 MIX
(dmax = 0.297)

4 MIX
(dmax = 0.592, L = 7.000)

6 MIX
(dmax = 0.184, L = 1.472)
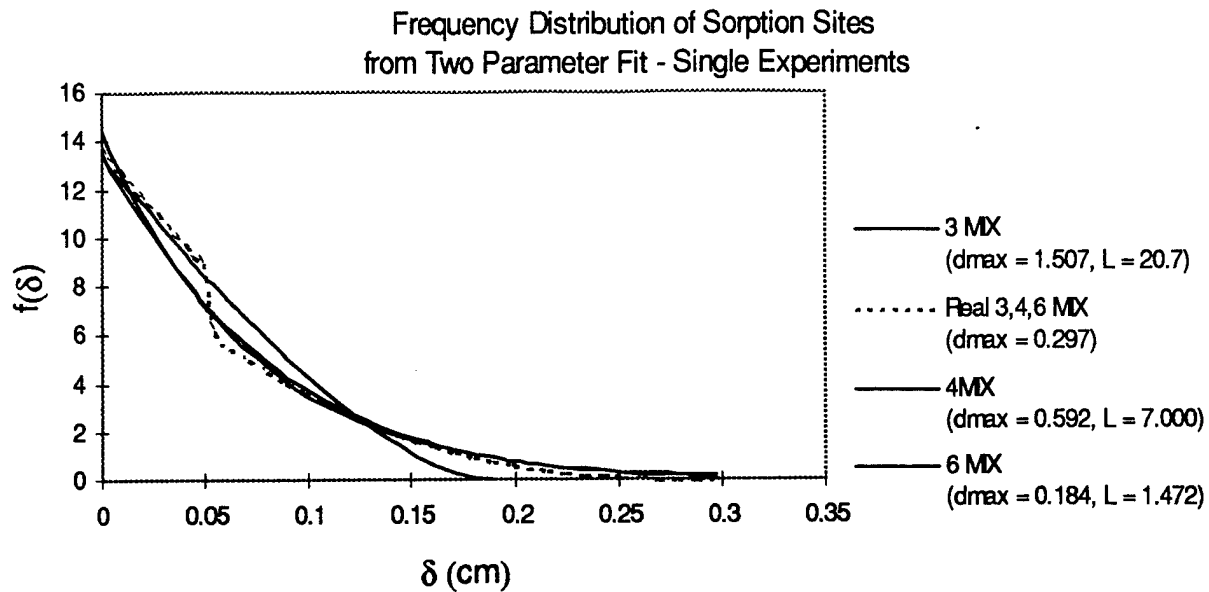
Figure D-11: Two parameter single experiment results, 3-6 MIX

Frequency Distribution of Sorption Sites
from Two Parameter Fit - Multiple Experiments

3&4 MIX
(dmax = 1.016, L = 13.246)

3,4,6 MIX
(dmax=0.440, L = 5.051)

Real 3,4,6 MIX
(dmax = 0.297)

4&6 MIX
(dmax = 0.287, L = 2.855)
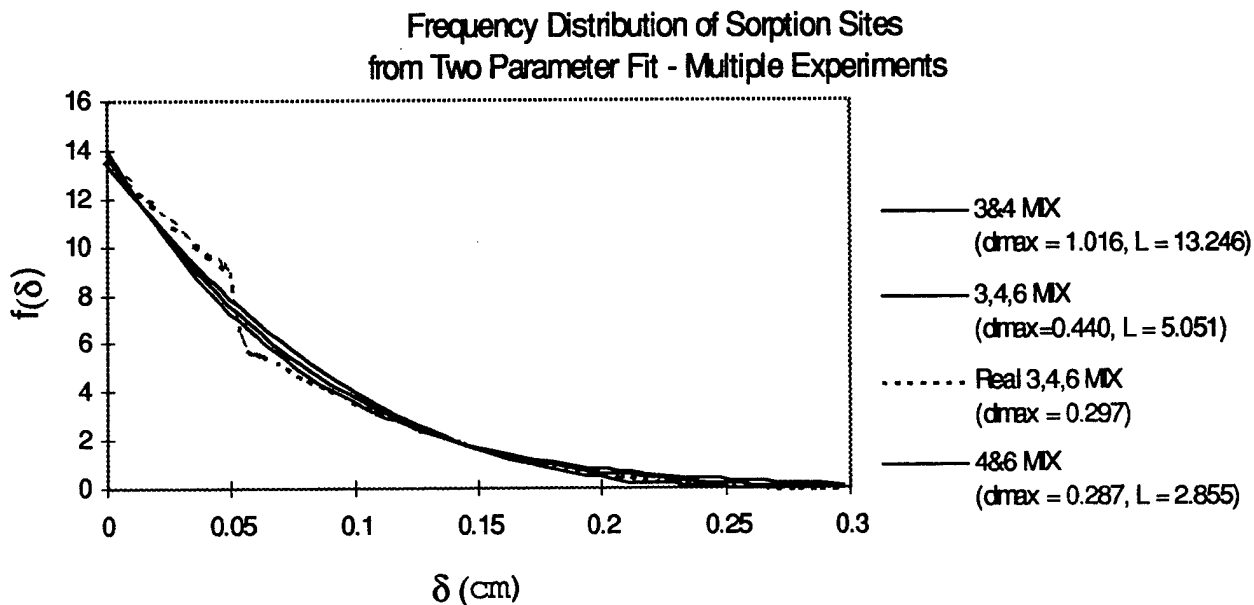
Figure D-12: Two parameter multiexperiment results, 3-6 MIX

Frequency Distribution of Sorption Sites
from Two Parameter Fit - Single Experiments

Real 3,4,6 MIX
(dmax = 0.297)

3 MIX
(dmax = 0.1.507, L = 20.7)

4MIX
(dmax = 0.592, L = 7.000)
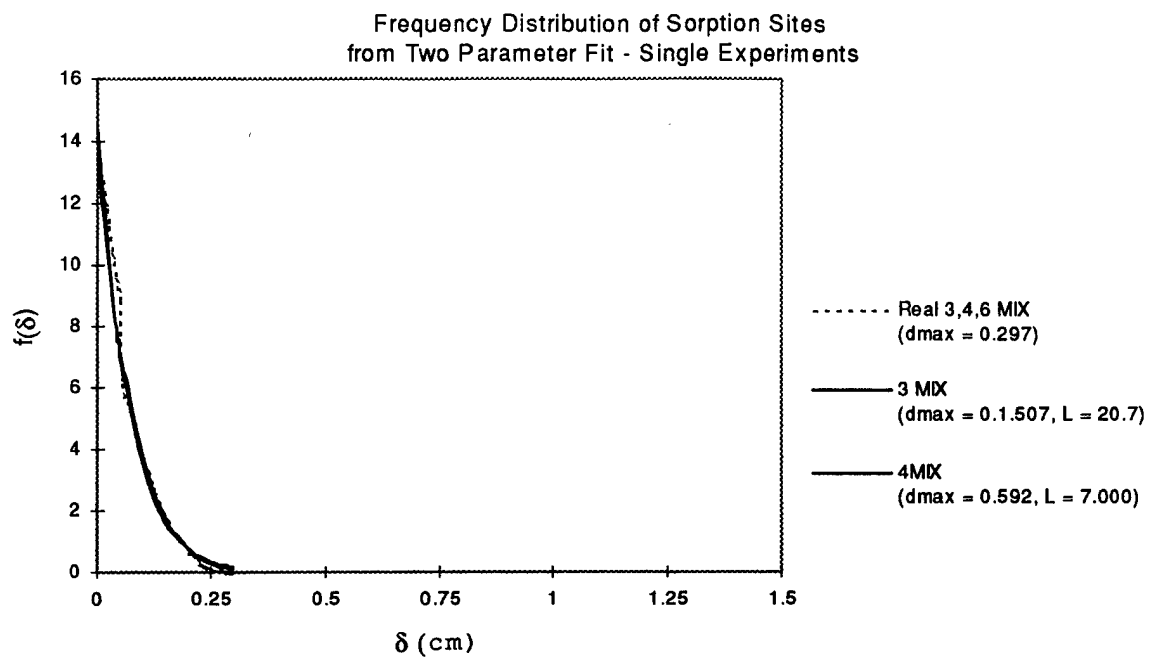
Figure: D-13: Two parameter single experiment results for 3 and 4 MIX, full scale

APPENDIX E
Data Files Used in MSS Model

```
TEST FOR MSSFIT:vial 1B
RKD      DEFF      DPATH       RLAM        XSS0        FAST
9.243 6.43E-9   0.297        2.0          0.0          0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,VLi, CLi)
2.038 20.153 0.714
5
1 432000.          1.32  0.   0.
2 860400.          0.662 0.   0.
3 1288800.         0.783 0.   0.
4 1738800.         0.754 0.   0.
5 2764800.         1.10  0.   0.
100 0
TIME(SECS)  CONCENTRATION(S/CL)
432000.          4.770
860400.          6.810
1288800.         7.738
1738800.         8.374
2764800.         8.978
3888000.         9.203


TEST FOR MSSFIT:vial 2B
RKD      DEFF      DPATH       RLAM        XSS0        FAST
9.243 1.0E-8    0.297        2.0          0.0          0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,VLi, Cli)
2.025 19.890 0.714
5
1 432000.          1.192 0.  0.
2 864000.          0.912 0.  0.
3 1296000.         0.828 0.  0.
4 1728000.         0.788 0.  0.
5 2764800.         1.043 0.  0.
100 0
TIME(secs)   CONCENTRATION(S/CL)
432000.          4.632
864000.          6.725
1296000.         7.734
1728000.         8.580
2764800.         9.169
3888000.         9.583
```

```
TEST FOR MSSFIT:vial 3B
RKD      DEFF      DPATH      RLAM        XSS0        FAST
9.243 1.0E-8    0.297        2.0         0.0         0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,V$_{Li}$, C$_{1i}$)
0.567 4.28 0.811
5
1 90000.         0.532 0. 0.
2 270000.        0.545 0. 0.
3 608400.        0.813 0. 0.
4 1209600.       0.583 0. 0.
5 2246400.       0.858 0. 0.
100 0
TIME(SECS)   CONCENTRATION(S/CL)
90000.           2.412
270000.          4.506
608400.          6.251
1209600.         7.958
2246400.         8.735
3456000.         9.287

TEST FOR MSSFIT:vial 4B
RKD      DEFF      DPATH      RLAM        XSS0        FAST
9.243 1.0E-8    0.297        2.0         0.0         0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS (Ms,V$_{Li}$, C$_{1i}$)
0.562 4.144 0.811
5
1 90000.         0.539 0. 0.
2 270000.        0.537 0. 0.
3 608400.        0.668 0. 0.
4 1209600.       0.591 0. 0.
5 2246400.       0.853 0. 0.
100 0
TIME(SECS)   CONCENTRATION(S/CL)
90000.           2.255
270000.          4.13
608400.          5.985
1209600.         7.74
2246400.         8.715
3456000.         9.061
```

```
TEST FOR MSSFIT:vial 5B
RKD     DEFF     DPATH    RLAM         XSS0         FAST
9.243 1.0E-8    0.297    2.0          0.0          0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0  1  0  0  0  0
CONSTANTS(Ms,V_{Li}, C_{li})
0.579 4.291 0.811
4
1 86400.        0.556 0. 0.
2 259200.       0.556 0. 0.
3 604800.       0.824 0. 0.
4 691200.       1.092 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
86400.          2.356
259200.         4.425
604800.         6.666
691200.         7.011
1436400.        8.919

TEST FOR MSSFIT:vial 6B
RKD     DEFF     DPATH    RLAM         XSS0         FAST
9.243 1.0E-8    0.297    2.0          0.0          0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0  1  0  0  0  0
CONSTANTS(Ms,V_{Li}, C_{li})
0.579 4.288 0.811
4
1 86400.        0.562 0. 0.
2 266400.       0.794 0. 0.
3 604800.       0.833 0. 0.
4 1296000.      0.599 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
86400.          2.068
266400.         4.288
604800.         6.448
1296000.        8.268
3110400.        9.215
```

```
TEST FOR MSSFIT:vial 1M
RKD      DEFF      DPATH      RLAM         XSS0           FAST
9.243 1.0E-8    0.249       2.0          0.0            0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS (Ms,$V_{Li}$, $C_{li}$)
1.984 18.917 0.714
5
1 435600.       1.417 0. 0.
2 864000.       0.691 0. 0.
3 1288800.      0.827 0. 0.
4 1738800.      0.767 0. 0.
5 2764800.      1.099 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
435600.         5.325
864000.         7.321
1288800.        8.199
1738800.        8.527
2764800.        9.185
3891600.        9.262


TEST FOR MSSFIT:vial 2M
RKD      DEFF      DPATH      RLAM         XSS0           FAST
9.243 6.43E-9   0.249       2.0          0.0            0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 0 0 0
CONSTANTS (Ms,$V_{Li}$, $C_{li}$)
1.995 20.268 0.714
5
1 435600.       1.304 0. 0.
2 864000.       0.683 0. 0.
3 1288800.      0.774 0. 0.
4 1738800.      0.771 0. 0.
5 2768400.      1.013 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
435600.         5.54
864000.         7.458
1288800.        8.148
1738800.        8.257
2764800.        9.196
3891600.        9.332
```

```
TEST FOR MSSFIT:vial 3M
RKD      DEFF     DPATH      RLAM        XSS0        FAST
9.243 6.43E-9   0.249      2.0         0.0         0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 0 0 0
CONSTANTS (Ms,V_{Li}, C_{1i})
0.505 4.29 0.811
5
1 90000.          0.532 0. 0.
2 270000.         0.568 0. 0.
3 608400.         0.756 0. 0.
4 1209600.        0.594 0. 0.
5 2246400.        0.859 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
90000.          2.774
270000.         4.705
608400.         6.506
1209600.        8.081
2246400.        8.792
3456000.        9.359

TEST FOR MSSFIT:vial 4M
RKD      DEFF     DPATH      RLAM        XSS0        FAST
9.243 1.0E-8    0.249      2.0         0.0         0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS (Ms,V_{Li}, C_{1i})
0.506 4.214 0.811
5
1 90000.          0.517 0. 0.
2 270000.         0.514 0. 0.
3 608400.         0.777 0. 0.
4 1209600.        0.601 0. 0.
5 2246400.        0.868 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
90000.            2.722
270000.           4.765
608400.           6.549
1209600.          8.156
2246400.          8.944
3456000.          9.141
```

TEST FOR MSSFIT:vial 5M
```
RKD     DEFF     DPATH    RLAM          XSSO          FAST
9.243 1.0E-8   0.249    2.0           0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,VLi, Cli)
0.51 4.328 0.811
4
1 86400.         0.536 0. 0.
2 259200.        1.148 0. 0.
3 604800.        0.8017 0. 0.
4 691200.        0.873 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
86400.                2.916
259200.               5.00
604800.               7.448
691200.               7.69
1436400.              9.266
```

TEST FOR MSSFIT:vial 6M
```
RKD     DEFF     DPATH    RLAM          XSSO          FAST
9.243 1.0E-8   0.249    2.0           0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS (Ms,VLi, Cli)
0.512 4.349 0.811
4
1 86400.         0.542 0. 0.
2 266400.        0.771 0. 0.
3 604800.        0.816 0. 0.
4 1296000.       0.588 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
86400.                2.61
266400.               5.00
604800.               7.04
1296000.              8.57
3110400.              9.01
```

```
TEST FOR MSSFIT:vial 1S
RKD       DEFF      DPATH       RLAM          XSS0          FAST
9.243 1.0E-8   0.1994       2.0           0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,Vli,Cli)
1.993 20.055 0.714
5
1 435600.        0.959 0. 0.
2 864000.        0.685 0. 0.
3 1288800.       0.785 0. 0.
4 1738800.       0.762 0. 0.
5 2768400.       1.063 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
435600.          6.620
864000.          8.347
1288800.         8.760
2764800.         9.207
3895200.         9.462

TEST FOR MSSFIT:vial 2S
RKD       DEFF      DPATH       RLAM          XSS0          FAST
9.243 1.0E-8   0.1994       2.0           0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,Vli,Cli)
2.002 20.187 0.714
5
1 435600.        0.927 0. 0.
2 864000.        0.678 0. 0.
3 1288800.       0.833 0. 0.
4 1738800.       0.795 0. 0.
5 2768400.       1.308 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
435600.          6.343
864000.          8.148
1288800.         8.76
1738800          8.794
2764800.         9.072
3895200.         9.476
```

```
TEST FOR MSSFIT:vial 3S
RKD      DEFF      DPATH       RLAM        XSS0          FAST
9.243 1.0E-8    0.1994        2.0         0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,Vli,Cli)
0.482 4.425 0.811
5
1 90000.         0.549 0. 0.
2 270000.        0.53  0. 0.
3 608400.        0.777 0. 0.
4 1209600.       0.584 0. 0.
5 2246400.       0.857 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
90000.              3.298
270000.             5.795
608400.             7.526
1209600.            8.62
2246400.            8.958
3456000.            9.078

TEST FOR MSSFIT:vial 4S
RKD      DEFF      DPATH       RLAM        XSS0          FAST
9.243 1.0E-8    0.1994        2.0         0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,Vli,Cli)
0.501 4.328 0.811
5
1 90000.         0.533 0. 0.
2 270000.        0.526 0. 0.
3 608400.        0.798 0. 0.
4 1209600.       0.576 0. 0.
5 2246400.       0.865 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
90000.              3.29
270000.             5.59
608400.             7.39
1209600.            8.56
2246400.            8.96
3456000.            9.15
```

```
TEST FOR MSSFIT:vial 6S
RKD      DEFF      DPATH      RLAM         XSS0           FAST
9.243 1.0E-8   0.1994       2.0          0.0            0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 1 0 0 0 0
CONSTANTS(Ms,Vli,Cli)
0.509 4.272 0.811
4
1 86400.          0.562 0. 0.
2 266400.         0.765 0. 0.
3 604800.         0.831 0. 0.
4 1296000.        0.597 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
86400.          3.07
266400.         5.654
604800.         7.64
1296000.        8.654
3110400.        9.275

TEST FOR MSSFIT:vial 1BM
RKD      DEFF      DPATH      RLAM         XSS0           FAST
9.243 6.43E-9  0.297        1.0      0.0          0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 1 0 0 0
CONSTANTS(Ms,Vli,Cli)
2.015 19.924 0.714
5
1 439200.         0.902 0. 0.
2 867600.         0.707 0. 0.
3 1289600.        0.803 0. 0.
4 1738800.        0.743 0. 0.
5 2768400.        1.055 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
439200.         5.229
867600.         7.093
1289600.        8.166
1738800.        8.638
2768400.        9.22
3895200.        9.671
```

```
TEST FOR MSSFIT:vial 2BM
RKD       DEFF      DPATH       RLAM          XSS0         FAST
9.243 6.43E-9    0.297       1.0           0.0          0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 1 0 0 0
CONSTANTS(Ms,Vli,Cli)
2.03 19.925 0.714
5
1 439200.        1.238 0. 0.
2 867600.        0.667 0. 0.
3 1289600.       0.586 0. 0.
4 1742400.       0.764 0. 0.
5 2772000.       1.066 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
439200.          5.237
867600.          7.269
1289600.         8.346
1742400.         8.587
2772000.         9.223
3895200.         9.555


TEST FOR MSSFIT:vial 3BM
RKD       DEFF      DPATH       RLAM          XSS0         FAST
9.243 6.430E-9    0.297       2.5570        0.0          0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 0 0 0
CONSTANTS(Ms,Vli,Cli)
0.523 4.245 0.811
5
1 93600.         0.563 0. 0.
2 273600.        0.532 0. 0.
3 615600.        0.772 0. 0.
4 1213200.       0.574 0. 0.
5 2250000.       0.872 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
93600.           2.75
273600.          4.89
615600.          6.68
1213200.         8.18
2250000.         8.73
3459600.         9.09
```

```
TEST FOR MSSFIT:vial 4BM
RKD     DEFF      DPATH       RLAM        XSS0        FAST
9.243 6.430E-9   0.297       2.0         0.0         0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 1 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.519 4.275 0.811
5
1 93600.        0.513 0. 0.
2 273600.       0.535 0. 0.
3 615600.       0.784 0. 0.
4 1213200.      0.591 0. 0.
5 2250000.      0.879 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
93600.          2.637
273600.         4.707
615600.         6.506
1213200.        8.089
2250000.        8.735
3459600.        8.924

TEST FOR MSSFIT:vial 6BM
RKD     DEFF      DPATH       RLAM        XSS0        FAST
9.243 6.43E-9    0.297       2.0         0.0         0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 1 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.514 4.390 0.811
4
1 90000.        0.576 0. 0.
2 266400.       0.764 0. 0.
3 604800.       0.846 0. 0.
4 1296000.      0.59 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
90000.          2.48
266400.         4.709
604800.         6.784
1296000.        8.495
3110400.        9.227
```

```
TEST FOR MSSFIT:vial 1ALL
RKD      DEFF     DPATH      RLAM        XSS0          FAST
9.243 6.43E-9    0.297      2.0         0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 1 0 0
CONSTANTS(Ms,Vli,Cli)
2.005 20.033 0.714
5
1 439200.        1.004 0. 0.
2 867600.        0.681 0. 0.
3 1292400.       0.778 0. 0.
4 1742400.       0.764 0. 0.
5 2772000.       1.032 0. 0.
100 0
TIME(secs)    CONCENTRATION(S/CL)
439200.          5.657
867600.          7.517
1289600.         8.452
1742400.         8.676
2772000.         9.159
3898800.         9.380


TEST FOR MSSFIT:vial 2ALL
RKD      DEFF     DPATH      RLAM        XSS0          FAST
9.243 6.43E-9    0.297      2.0         0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 1 0 0
CONSTANTS(Ms,Vli,Cli)
1.975 25.562 0.714
5
1 439200.        1.16  0. 0.
2 867600.        0.66  0. 0.
3 1292400.       0.795 0. 0.
4 1742400.       0.807 0. 0.
5 2772000.       1.021 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
439200.          5.589
867600.          7.521
1289600.         8.434
1742400.         8.656
2772000.         9.116
3895200.         9.578
```

```
TEST FOR MSSFIT:vial 3ALL
RKD      DEFF      DPATH        RLAM          XSS0          FAST
9.243 6.430E-9   0.297         2.0           0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 1 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.52 4.27 0.811
5
1 93600.         0.55  0. 0.
2 273600.        0.527 0. 0.
3 612000.        0.771 0. 0.
4 1213200.       0.596 0. 0.
5 2250000.       0.838 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
93600.        2.774
273600.       4.89
612000.       6.042
1213200.      8.109
2250000.      8.729
3459600.      8.975


TEST FOR MSSFIT:vial 4ALL
RKD      DEFF      DPATH        RLAM          XSS0          FAST
9.243 6.430E-9   0.297         2.0           0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.523 4.267 0.811
5
1 97200.         0.55   0. 0.
2 277200.        0.467  0. 0.
3 612000.        0.8313 0. 0.
4 1213200.       0.601  0. 0.
5 2250000.       0.844  0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
97200.        2.562
277200.       4.78
612000.       6.591
1213200.      8.281
2250000.      8.899
3459600.      9.19
```

```
TEST FOR MSSFIT:vial 6ALL
RKD     DEFF      DPATH      RLAM       XSS0        FAST
9.243 6.43E-9   0.297      2.0        0.0         0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.526 4.262 0.811
4
1 90000.        0.568 0. 0.
2 266400.       0.783 0. 0.
3 604800.       0.823 0. 0.
4 1296000.      0.588 0. 0.
100 0
TIME(SECS)    CONCENTRATION(S/CL)
90000.          2.461
266400.         4.72
604800.         6.774
1296000.        8.29
3110400.        9.129

TEST FOR MSSFIT:vial 1mixB
RKD     DEFF      DPATH      RLAM       XSS0        FAST
9.243 6.43E-9   0.297      2.0        .0.0        0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 1 1 0 0
CONSTANTS(Ms,Vli,Cli)
1.721 13.381 0.714
5
1 86400.        0.762 0. 0.
2 172800.       0.690 0. 0.
3 266400.       0.814 0. 0.
4 345600.       0.68  0. 0.
5 453600.       0.73  0. 0.
100 0
TIME(secs)    CONCENTRATION(S/CL)
86400.          3.101
172800.         5.256
266400.         6.808
345600.         7.587
453600.         8.285
1306800.        10.42
```

```
TEST FOR MSSFIT:vial 2mixB
RKD       DEFF      DPATH        RLAM          XSS0          FAST
9.243 6.43E-9    0.297        2.0           0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0  0  1  1  0  0
CONSTANTS(Ms,Vli,Cli)
1.672 13.743 0.714
5
1 86400.          0.68  0. 0.
2 176400.         0.713 0. 0.
3 266400.         0.761 0. 0.
4 345600.         0.757 0. 0.
5 453600.         0.748 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
86400.            3.137
176400.           5.37
266400.           6.676
345600.           7.513
453600.           8.215
1306800.          10.29

TEST FOR MSSFIT:vial 3mix
RKD       DEFF      DPATH        RLAM          XSS0          FAST
9.243 6.430E-9   0.297        2.0           0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0  0  1  1  0  0
CONSTANTS(Ms,Vli,Cli)
0.431 4.272 0.811
5
1 97200.          0.535      0. 0.
2 277200.         0.56       0. 0.
3 615600.         0.7923     0. 0.
4 1216800.        1.185      0. 0.
5 2253600.        0.589      0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
97200.            3.331
277200.           5.019
615600.           6.479
1216800.          7.943
2253600.          8.659
3463200.          9.068
```

```
TEST FOR MSSFIT:vial 4mix
RKD      DEFF      DPATH      RLAM      XSS0      FAST
9.243 6.430E-9   0.297       2.0       0.0       0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 1 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.424 4.205 0.811
5
1 97200.          0.537 0. 0.
2 277200.         0.677 0. 0.
3 615600.         0.749 0. 0.
4 1216800.        0.595 0. 0.
5 2253600.        0.833 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
97200.           3.089
277200.          4.983
615600.          6.656
1216800.         8.128
2253600.         8.745
3463200.         8.982

TEST FOR MSSFIT:vial 6Mix
RKD      DEFF      DPATH      RLAM      XSS0      FAST
9.243 6.43E-9    0.297       2.0       0.0       0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 1 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.433 4.257 0.811
4
1 90000.          0.558 0. 0.
2 266400.         0.783 0. 0.
3 604800.         0.844 0. 0.
4 1296000.        0.597 0. 0.
100 0
TIME(SECS)     CONCENTRATION(S/CL)
90000.           3.086
266400.          5.395
604800.          7.316
1296000.         8.721
3110400.         9.668
```

```
TEST FOR MSSFIT:vial 1GB
RKD      DEFF      DPATH      RLAM         XSS0          FAST
9.243 6.43E-9    0.049       0.01         0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0  0  0  1  0  0
CONSTANTS(Ms,Vli,Cli)
0.629 11.876 0.714
5
1 86400.         0.774 0. 0.
2 172800.        0.707 0. 0.
3 266400.        0.780 0. 0.
4 345600.        0.778 0. 0.
5 453600.        0.728 0. 0.
100 0
TIME(secs)     CONCENTRATION(S/CL)
86400.           5.023
172800.          7.486
266400.          8.521
345600.          8.942
453600.          9.39
1306800.         9.898


TEST FOR MSSFIT:vial 2GB
RKD      DEFF      DPATH      RLAM         XSS0          FAST
9.243 6.43E-9    0.049       0.01         0.0           0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0  0  0  1  0  0
CONSTANTS(Ms,Vli,Cli)
0.632 11.757 0.714
5
1 86400.         0.713 0. 0.
2 176400.        0.692 0. 0.
3 266400.        0.588 0. 0.
4 345600.        0.765 0. 0.
5 453600.        0.711 0. 0.
100 0
TIME(sec)     CONCENTRATION(S/CL)
86400.           5.101
176400.          7.591
266400.          8.316
345600.          8.885
453600.          9.46
1306800.         9.871
```

```
TEST FOR MSSFIT:vial 7G
RKD       DEFF      DPATH       RLAM        XSS0           FAST
9.243 6.43E-9    0.049       0.01        0.0            0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.205 4.406 0.811
3
1 86400.        0.926 0. 0.
2 262800.       0.851 0. 0.
3 604800.       0.586 0. 0.
100 0
TIME(SECS)      CONCENTRATION(S/CL)
86400.          5.157
262800.         7.736
604800.         8.942
1220400.        9.076

TEST FOR MSSFIT:vial 8G
RKD       DEFF      DPATH       RLAM        XSS0           FAST
9.243 6.43E-9    0.049       0.01        0.0            0.0
1 MEANS FIT PARAMETER, 0 MEANS KEEP IT FIXED
0 0 0 1 0 0
CONSTANTS(Ms,Vli,Cli)
0.219 4.334 0.811
3
1 86400.        0.813 0. 0.
2 262800.       0.834 0. 0.
3 604800.       0.582 0. 0.
100 0
TIME(SECS)      CONCENTRATION(S/CL)
86400.          5.303
262800.         7.78
604800.         8.94
1220400.        9.14
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2192

VITA.

Captain Thomas Peter de Venoge was born in Queens, New York, 13 May 1964. He was raised in McLean, Virginia with eight siblings and attended schools in the Northern Virginia Area. Following graduation from Bishop Denis J. O'Connell High School in Arlington, Virginia, he went on to matriculate at the Virginia Military Institute (VMI), Lexington, Virginia, in August 1982, and later received a Bachelor of Science degree in Civil Engineering in May,1986. He was commissioned a Second Lieutenant in the United States Air Force, Biomedical Sciences Corps, in August, 1986 and reported to Williams Air Force Base (AFB), Arizona for his first duty assignment as Chief, Bioenvironmental Engineering, in January 1987. He was assigned to Soesterberg Air Base, The Netherlands, for three years in September, 1990, serving in the same title. Upon returning to the United States in September, 1993, he was stationed at Tyndall AFB, Florida, where he worked as a project manager for environmental remediation technology development until departing for a Master of Science program in Environmental Management and Engineering at the Air Force Institute of Technology, Wright-Patterson AFB, Ohio, in May 1995. He is married to the former Debra Ann Fancsali, and is the proud father of two future VMI cadets and scientists: Amy Marie, and Julie Anna, ages 1 and 5.

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13. ABSTRACT (Maximum 200 words)

Existing sorption models often fail to describe grain scale sorption because of an inability to define the diffusion domain. A proposed improved model required testing to determine model validity. The testing method used a synthetic media of known geometry such that the distribution of sorption sites was known. Sorption rate data was obtained using batch experiments with the media. Data was used in comparison against model predicted rates. Fitted sorption site distributions were compared to real distributions obtained by controlling sorbent geometries. Comparison determined model performance in fitting known distributions. The focus of this study was to, 1) determine what protocols are necessary to ensure consistent chemical and physical properties of a synthetic media for sorption studies, 2) determine if the proposed model can predict the known shape parameters describing the frequency distribution of sorption sites by using the rate data obtained from sorption studies, and 3) validate the model

Model performance was encouraging for simultaneous fitting of two shape parameters. Simulations resulted in sorption site distributions similar to the known distributions. This model is an improvement over other diffusion models where geometries are assumed to be spherical. Prediction of real soil sorption site distributions may be possible

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